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THE DETERMINATION OF ORGANIC COMPOUNDS IN LOW CONCENTRATIONS.

I. DETERMINATION OF ORGANIC HALOGEN.

II. SODIUM PEROXIDE AS A REAGENT IN MICROCHEMICAL ANALYSIS.

III. SAMPLING OF GAS CONCENTRATIONS.

BY

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May 15th 1919.

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY

SUPERVISION BY Herbert August Winkelmann

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BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR

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I also wish to express my gratitude to the following men, who as observers, rendered invaluable assistance in perfecting the methods of sampling and determination of low gas concentrations: Wm. S. Bacon, W. R. Kirner, C. Rascher, W. A. Landeman, R. G. Huffman, M. Guren, O. V. Schaffer, R. L. Noble, W. Haskins, H. R. Walls, F. M. Crawford.

Herbert A. Winkelmann.

I. INTRODUCTION.

The determination of organic compounds in low concentrations under field conditions involved a careful study of the reactions of each compound. A method of determination to be accurate had to be thoroughly tested under conditions as similar to field conditions as possible. It was necessary to determine the possible interferences and limits of each method developed. The compounds used contained a halogen or nitrogen and sometimes both in the molecule. The methods of analysis developed were used with the purpose of determining the halogen or nitrogen compound resulting from the decomposition of the original compound by means of suitable absorbing solution. The organic compounds used included compounds which are gases, liquids and solids at ordinary temperatures. Gas concentrations of liquids and solids were produced by the high explosive force of the explosive used, and by the temperature produced on detonation. The term gas as it is used includes concentrations produced from gases, liquids, and solids. In liquids there is both the liquid and gaseous phase, and in solids, a gaseous and particulate phase and possibly a liquid phase to be considered. The choice of compounds used depends upon their stability on detonation. The compounds used were not appreciably composed on detonation, if the amount of explosive was properly varied for each compound. The determination of a concentration depending on a halogen determination

means nothing if the compounds are partially decomposed. These facts were all essential in choosing the correct method of analysis, and method of sampling.

The sampling of gas concentrations in the field presented many problems that required satisfactory solutions if interpretations were to be made on the analysis. With a standard method of sampling, the procedure of each method of analysis was readily applied to the analysis of field samples. The samples of gas were collected by means of evacuated bottles with the Automatic Electrical Sampling Apparatus. On releasing the vacuum of the bottle in a gas concentration a sample of gas was drawn in and confined in the bottle. Due to the very low concentrations obtained in the field, it was necessary to introduce dilute absorbing solutions into the bottles to decompose the gas. It was necessary that complete absorption and decomposition take place in the cold. This was hastened by thoroughly shaking the bottle. Numerous rapid and accurate methods of analysis for the determination of organic halogen using dilute absorbing solutions were developed.

Sodium peroxide in dilute solutions was introduced for the decomposition and analysis of organic halogen. Its use was extended as a reagent for determining nitro groups microchemically.

Quantitative methods for the determination of halogen in the following substances were worked out and studied: Chloropicrin, Brom-benzyl cyanide, Dichlordiethyl sulphide, Trichloromethyl chloroformate, Chloracetophenone, D.M., Di-

chlordimethyl ether and benzal chloride. Methods for the determination of the following mixtures were introduced: Chloropicrin and Dichlordiethyl sulphide; chloropicrin and trichloromethyl chloroformate; cyanogen chloride and phosgene.

A method of determining chloropicrin and trinitrotoluene michrochemically gave very satisfactory results.

The automatic sampling of gases by means of the electro magnet and evacuated bottle was so satisfactory that a description of the apparatus and its use is given. A wide application of this method of sampling may be made for sampling of gases under different conditions and formany other purposes.

This study is divided into three parts:

1. The Determination of Organic Halogen.
2. Sodium Peroxide as a Reagent in Michrochemical Analysis.
3. Sampling of gases in low concentrations.

II. HISTORICAL.

The methods outlined in the literature for the determination of halogens in organic compounds cannot be carried out rapidly. The use of special apparatus or large amounts of reagent and often both are necessary. A fair sized sample of the substance must also be taken for analysis. A bomb furnace, fusion method or combustion method must be used. To this class belong the methods of Cairius, Liebig, Volhard, Pringsheim and Reid. Donau determined halogens in small amounts of organic substances[1] by decomposing them in a micro bomb.

These methods could not be applied on low concentrations of organic compounds. Neither the apparatus nor the methods could be applied due to the fact that heat and large amount of reagent for decomposition are necessary. The reagents such as lime, soda lime, and sodium hydroxide are not easily obtained chloride free.

The use of dilute solutions of the reagents was the first procedure tried out. Weyle (page 45) states that in very few instances can the halogen in organic compounds be determined directly. Silver nitrate often precipitates the halogen of a halogen acid salt. Acid chlorides are hydrolysed in dilute solution and may be titrated with standard silver nitrate solution using potassium chromate as an

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[1] Monatsch 33 - 169 - 76.

indicator.[1] By the action of alcoholic potassium hydroxide the halogen is split off from many organic compounds. Halogen substituted acids when treated with the sodium amalgam and water give the sodium salt of the halide.[2] Ziesel's method of determining Methoxygrups may be applied to the determination of halogens in compounds such as alkyl iodide, etc.[3]

Lowenherz[4] decomposed organic halogen compounds with sodium amalgam in alcohol. The method of Stepanov[5] in which he uses sodium in absolute alcohol to decompose organic halogens has also been used by Lowenherz.[6] Bacon[7] modified Stepanov's method by using sodium ethylate on organic compounds. Walker and McCrae[8] recommend 10% more sodium to Bacon's modification.

The use of sodium amalgam in alcohol, and sodium in absolute alcohol in ultimate analysis suggested their use as absorbing solutions for the decomposition of low gas concentrations. The amount of substance present being small, the concentration of the absorbing solution was decreased as much as possible. The absorbing solutions were used on substances that were insoluble in water, or whose solubility was not over 0.1%. Some substances were used that were hydrolyzed

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1. H. Meyer M. 22 109, 415 (1901).
2. Kekule A. Supl. I, 340 (1861).
3. M. 6 989 (1885); M. 7 406 (1886).
4. Zt. Physikal Chem. 40, 399 (1902).
5. Ber. 39, 4056 (1906).
6. Zt. Physikal Chem. 36, 469 (1901).
7. J.A.C.S. 31, 49 (1909).
8. J.A.C.S. 33, 598.

by water. It was necessary to determine by experimentation whether an oxidation or reduction reaction was the satisfactory one to use, or whether a neutral salt was equally desirable. The action of the following absorbing solutions on the above mentioned compounds were studied for complete or partial decomposition: aqueous and alcoholic sodium hydroxide and sodium carbonate, sodium ethylate, sodium thiosulphate, aqueous and alcoholic sodium peroxide, sodium amalgam in alcohol, alcoholic sodium sulphite and potassium permanganate.

No mention has been made of the use of dilute solutions of sodium peroxide in Organic analysis. Sodium peroxide was first used in the fusion method by Hempel[1] and Clark[2] for the determination or organic halogen. Hempel recognized its superiority in the fusion method over other oxidizing agents on account of its purity and rapidity of action. The method was later modified by Pringsheim[3]. The use of sodium peroxide in dilute solutions, in the oxidation of organic compounds makes the use of sodium peroxide more important in the field of Organic Analysis than it has been in the past.

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1. Hempel, Zt. Anorg. Chem. (1892) 3, 193.
2. J. Chem. Soc. Trans. (1893) 1079.
3. Ber. 38, 2459, (1905); Ber. 41, 4267 (1908).

III. DISCUSSION.

The conditions which are carefully controlled in the laboratory in studying the effectiveness of a gas concentration cannot be controlled in the field. The results obtained in the laboratory must be applied under field conditions to determine whether the substance is fully as effective as it was in the laboratory experiments. Different methods of sampling and analysis must be developed and used.

The diffusion of the molecules of any gas in air is increased by convection currents, due to differences in the temperature of the soil and the air above it, andstill more by the winds. The concentration effective under atmospheric conditions must be exceedingly high unless the gas is considerably heavier than air. According to Graham's law, the rate of diffusion of the molecules of any gas is inversely proportional to the square roots of their densities. The wind must have the right strength and direction or the gas cloud will not traverse the desired sector. The effect of wind currents and eddies, contour of the land, (that is, the effect of valleys and woods) and the effect of humidity and temperature have a direct influence on the effectiveness of a concentration. The optimum wind velocity is 4-12 miles per hour, and assuming a velocity of 6 miles an hour, the cloud travels at the rate of about 9 feet per second.

The duration of a concentration, except in case of continuous fire is comparatively short. The sampling of

gases must be quick and efficient, and this is obtained by taking a series of instantaneous samples automatically. Samples taken over a longer period do not represent the concentration at any exact moment, and the sample also represents a concentration of another part of the moving cloud. Concentrations in the field as determined by their effect on men and animals are not high, a concentration of 1 part in 10,000 may produce immediate casualties without protection. The average concentration obtained on the field is much lower. The determination of organic compounds under these conditions is very much lower than the amounts ordinarily considered.

The determination of concentrations obtained in the field requires an accurate analysis. The quantitative determination of organic compounds was studied in a new light as accurately as experimental errors would allow. This is particularly important because the substances are toxic and effective in these low concentrations and also in lower concentrations than can be accurately determined.

The concentrations that may be obtained vary with the vapor pressure of the substance at the given temperature. A high vapor pressure will give a high maximum concentration and makes it possible to obtain a higher concentration for analysis. When the vapor pressure is very low the highest obtainable concentration is often so low that its determination is difficult unless a large sample is collected. In case of solids the particulate phase is more important than the gaseous phase. The concentration is produced by using a "booster" which, due to the explosive force, disperses the

solid in a very finely divided state. The substances being in the atomized or particulate phase are sampled and analyzed in the regular way. Very low concentrations were effective before the eye or nose could detect them, others were effective in such low concentrations that an accurate estimation seemed out of the question. This is especially true of the solid substances. The use of colorimetric methods of analysis were necessary for the very low concentrations.

A careful study of the methods of determining various organic compounds was made. The compounds used contained either chlorine, bromine, or nitrogen, and the problem was to use a suitable absorbent which would decompose the substance and give the above elements in an ionized form that could be readily determined. The higher the per cent of chlorine, bromine, or nitrogen in the compound the lower was the concentration that could be determined. Hence the percentage of these elements in a compound was one of the limitations for determining low concentrations.

Methods of oxidation and reduction in alkaline and acid solution, and reactions with neutral salts were carefully tried out for the decomposition of the various compounds. For the decomposition, a standard amount of 50 c.c. of absorbing solution is always used. A dilute absorbing solution is used whenever possible. Thelower the amount of reagent necessary to reduce or oxidize a compound, the lower is the blank determination. Alcoholic solutions of absorbents are desirable when concentrations of gases are being aspirated through absorbing solutions. The alcohol is used as a

solvent to allow the absorbing solution to completely decompose the gas. In the methods for the analysis of field samples, aqueous solutions have been used wherever possible. Using an evacuated bottle for sampling, the gas is confined in the container for the action of the absorbing solution, and intimate contact between the gas and absorbing solution is obtained by thorough shaking. The use of alcohol has been omitted wherever possible because its use lengthens the procedure due to the fact that it must be removed by boiling before proceeding with the analysis.

The criteria of a quantitative method for determining a low gas concentration of a compound are: (1) The absorbing solution must completely decompose the substance; (2) Decomposition must take place in the cold. As an alternative alcohol may be used as an absorbentand the solution refluxed for decomposition; (3) An aqueous solution of the absorbent should be used. The decomposition is as effective as with alcoholic solutions in most cases, and the procedure is greatly shortened. (4) The shorter the method themore efficiently it can be applied in analyzing a large number of samples; (5) A volumetric or micro-chemical method only, should be used.

In using Volumetric methods of analysis for chlorine or bromine 0.3 c.c. of N/100 silver nitrate is used as the limit or accuracy. Below this value is considered a trace, as the end point is too indefinite. Whenever standard solutions of Iodine could be used lower concentrations were

determined because a very definite end point is always obtained with 0.05 c.c. of 0.02N solution of Iodine.

The size of evacuated bottle which gave a good sample and was easy to handle in large numbers was a 2½ liter bottle. In very low concentrations a better sample is obtained by using a larger bottle. The larger bottles, however, were not as easy to handle in large numbers. The advantage of the evacuated bottle for sampling is the fact that in a drifting concentration the exact concentration at a point for a given period, can be determined by a series of samples. Concentrations of some compounds which are strong enough to produce casualties are often too low to be accurately determined from small samples. Such concentrationsare best obtained by taking an average sample over a definite period. By this method accurate results were obtained with low concentrations.

Direct Method.

In developing a method of analysis of a compound the Direct Method of decomposition and analysis was always tried out first. The sample of liquid was always weighed out in a sealed glass bulb, thus avoiding an errors in taking the sample. If the sample was solid it was either weighed out directly, or an aliquot of the compound in some solvent was measured out. The sample was placed in a 500 c.c. glass stoppered bottle. Various strengths of absorbing solution were used to determine the best one to use. Several glass beads were added to facilitate breaking the glass bulb by

shaking. The bottle was shaken for ½ hour and analyzed immediately, or allowed to stand for a certain period. The contents of the bottle were transferred to an Erlenmeyer flask and acidified with concentrated nitric acid. When alcohol was present, it was boiled off before acidifying. The chloride or bromide was then determined by adding an excess of standard silver nitrate. The silver chloride was coagulated by warming the solution, filtered off, and washed. The filtrate was cooled. The excess silver was titrated with standard sodium thiocyanate, using 2 c.c. of ferric alum as the indicator. A blank determination was alwaysmade.

Vacuum Bottle Method.

To duplicate field sampling as nearly as possible the Vacuum Bottle Method of analysis was also used. The 2½-liter acid bottle was the easiest available bottle, also the most rugged to withstand hard usage. It was used until the L.P.G. Vacuum Bottle was designed.

The 2½-liter acid bottle was fitted with a No. 23 "Longshape" one-hole rubber stopper. A piece of glass tubing about 4 inches long having a 2 mm. wall and a diameter of 10 mm. was inserted into the stopper. A piece of pressure tubing about 3" - 3½" long with a clamp attached was fitted on the glass tubing. A weighed sample in a glass bulb was placed in the bottle with a few glass beads to facilitate breaking the bulb. The stopper was tightly inserted into the neck of the bottle by means of a Stopper Holder designed for the purpose.

The bottle was then evacuated and the bulb broken. Any liquid having a normally high vapor pressure was immediately vaporized. When the vapor pressure was low or the samples were large, they vaporized more slowly. A solid was only appreciably affected when an alcoholic solution was used, in this way giving better dispersion. In this method the absorbing solution had to decompose the compound in the bottle exactly as under field conditions. After decomposition the desired method of analysis was applied for halogens or other elements and groups. If a method gave satisfactory results with the Direct and Vacuum Bottle method, it was used for the determination of a concentration from a gas chamber as a final test for its accuracy. This was as close to field conditions as could be obtained in the laboratory.

In the experimental work, reference will be made quite frequently to the Direct and Vacuum Bottle Method of decomposition.

In the L.P.G. Vacuum bottle, the rubber stopper of the 2½-liter acid bottle was eliminated, and the L.P.G. bottle was used with a rubber tubing connection between the tip and the bottle proper, or a glass tip was sealed on the bottle directly before evacuating. (See Photograph No. 2.) Losses of Vacuum did not occur with this bottle on standing and it was easier to handle.

It is essential that a blank determination be made with each series of determinations; especially is this important in all low concentrations.

Complete contact of the gas in the bottle with the absorbing solution was only obtained by thorough shaking. Thorough shaking of the bottle and allowing it to stand over night was a very good, reliable and convenient method to use. By increasing the time of shaking and making it continuous, the time of standing necessary was in most cases shortened to several hours. The shaking in the course of this work was performed on a shaking wheel. Comparative results were thus obtained because each bottle received identically the same treatment.

The concentration of a compound may be expressed in several different ways. It may be expressed as milligrams per liter. This method is a convenient one to use and is not based on any assumptions. The concentration may also be expressed in Parts per Million by Volume and from this the concentration or volume of air containing one volume of gas is readily obtained. The term, parts per million, is calculated from the gram molecular volume, and assumes that the compound obeys the gas laws. This assumption is not true because it is known that compounds having a low boiling point and high vapor pressure do not obey the gas laws; and high boiling substances of low vapor pressure, as well as solids do not obey the gas law at all. All three methods of expressing concentrations are given throughout this work because no other form of expressing concentration has been adopted.

Chloracetophenone, D. M., chloropicrin and brombenzyl cyanide are insoluble in water and are not hydrolyzed

by it. Dichlordiethyl sulphide is 0.1% soluble in water, but is slowly hydrolyzed by cold and very easily by hot water. Benzal chloride is decomposed by water at 150° C, and is not hydrolyzed in the cold. Trichloromethyl chloroformate is slowly hydrolyzed in the presence of water, and the reaction is quite rapid at 100° C. Dichlordimethyl ether is slowly hydrolyzed by water. Phosgene and cyanogen chloride are very easily decomposed by water. The compounds studied include solids and liquids unaffected by water, liquids insoluble in water but hydrolyzed by it, liquids slowly hydrolyzed by water, and compounds which are gaseous at ordinary temperatures and very easily decomposed. The compounds include very stable compounds which are quantitatively decomposed by the dilute absorbing solutions used.

The following standard methods have given the best results and will be referred to throughout this study.

SODIUM PEROXIDE METHOD.

Procedure.

Solutions:

¼% to 5% Sodium peroxide
Concentrated Nitric Acid.
N/10 to N/100 Silver Nitrate
N/10 to N/100 Sodium Thiocyanate.
Ferric Alum indicator.

Collect a sample, if in the gaseous phase, in an evacuated bottle. If a liquid, weigh in a glass bulb and use

Direct Method of Analysis; if a solid use an alcoholic solution or weigh out sample directly, using the Direct method. Introduce 50 c.c. of absorbing solution and shake thoroughly for ½ hour and proceed with the analysis; or shake at intervals and allow to stand over night. After decomposition, transfer the contents of the bottle to an Erlenmeyer flask, carefully washing out the bottle. Acidify with 5 c.c. concentrated nitric acid. Add an excess of standard silver nitrate solution, warm to coagulate the silver halide, filter, wash and cool. Add 2 c.c. of ferric alum as indicator and titrate the excess silver nitrate with standard sodium thiocyanate. Make a blank determination at the same time that the analysis is made.

ALCOHOLIC SODIUM SULPHITE METHOD.

Solutions:

3% Sodium Sulphite, in 30% alcohol
Concentrated Nitric Acid.
N/10 or N/100 Silver Nitrate
N/10 or N/100 Sodium Thiocyanate
Ferric Alum indicator.

Sodium Sulphite is a neutral salt, although in solution it acts both as a neutral salt and as a reducing agent. The alcoholic sodium sulphite method was in use before the sodium peroxide method was worked out. The disadvantage of the alcoholic sodium sulphite method is the time consumed in making the analysis. The alcohol and the sulphur dioxide must be boiled off, which consumes considerable time

when compared with the aqueous sodium peroxide method. When complete decomposition occurs, the alcoholic sodium sulphite is an accurate method of determination.

Add 50 c.c. of the alcoholic sodium sulphite solution to thebottle containing substance to be decomposed. Shake thoroughly and allow to stand over night. Transfer the solution to an Erlenmeyer flask and boil off the alcohol. Acidify with 5 c.c. of concentrated nitric acid. Add an excess of standard silver nitrate solution. Carefully boil off the sulphur dioxide that is formed. Filter off the precipitate of silver halide, wash and cool. Add 2 cc. of ferric alum as indicator to the filtrate and titrate the excess silver nitrate with standard sodium thiocyanate solution. Make a blank determination at the same time that the analysis is made.

SODIUM ETHYLATE METHOD.

Solutions:
1 - 5% Sodium Ethylate.
Concentrated Nitric Acid (Sp. Gr. 1.42)
N/10 to N/100 Silver Nitrate
N/10 to N/100 Sodium Thiocyanate.
Ferric Alum Indicator.

The sample is decomposed with 25 c.c. of the sodium ethylate solution. Shake thoroughly and allow the bottle to stand over night. After decomposition, transfer the contents of the bottle into an Erlenmeyer flask taking care that the solution and blank are made up to the same

volume. Evaporate off the alcohol. Cool and add 10 c.c. of concentrated nitric acid. Add an excess of standard silver nitrate and warm to coagulate the percipitate of silver halide, filter, wash and cool. Add 2 cc. of ferric alum as indicator and titrate the excess silver nitrate with standard sodium thiocyanate. Make a blank determination along with the analysis.

SODIUM HYDROXIDE AND SODIUM CARBONATE METHODS.

Solutions:

½% - 10% Sodium Hydroxide or Sodium Carbonate
Concentrated Nitric Acid (Sp. Gr. 1.42)
N/10 to N/100 Silver Nitrate
N/10 to N/100 Sodium Thiocyanate.
Ferric Alum Indicator.

Whether the Direct or Vacuum Bottle Method of decomposition be used, the bottle is shaken with 50 c.c. of the aqueous or alcoholic absorbing solution and allowed to stand over night. Transfer the contents of the bottle to an Erlenmeyer flask and boil off the alcohol. Acidify with concentrated nitric acid. Add an excess of standard silver nitrate. Warm to coagulate the silver halide, filter, wash and cool the filtrate. Titrate the excess silver nitrate with standard sodium thiocyanate using 2 cc. of ferric alum as indicator. Make a blank determination at the same time that the analysis is made.

The procedure for aqueous sodium hydroxide or sodium carbonate is the same as for alcoholic solutions, except that there is no alcohol to boil off.

I. DETERMINATION OF HALOGEN IN ORGANIC COMPOUNDS.

IV. EXPERIMENTAL.

Chloropicrin.

Sodium peroxide has been used in Organic Analysis as a gross reagent. Its use in dilute solutions for the decomposition of chloropicrin required some experimentation and it was found that the results were as accurate with the weaker as with the stronger solutions. Alcohol was first used as a solvent for the chloropicrin in the absorbing solutions. The results obtained with aqueous solutions of sodium peroxide, showed that the presence of alcohol was unnecessary. Fresh solutions of peroxide were prepared for every series of determinations that were carried out.

Action of Alcoholic Sodium Peroxide Solution on Chloropicrin.

An alcoholic solution of sodium peroxide was first used in the decomposition of chloropicrin. The presence of alcohol was found necessary in absorption methods whenever the air containing the substance in the gaseous phase was aspirated through wash bottles containing the absorbing solution. The Direct Method of decomposition was first used, with 50 cubic centimeters of the absorbing solution. The samples were shaken at intervals and were analyzed at the expiration of the time indicated in the table, according to the standard sodium peroxide method. The purity of the sample used was 99.04 per cent.

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TABLE 1.

3.6% Sodium Peroxide in 50% Alcohol.

Time	Gm. Chloropicrin taken	Gm. Chloropicrin found	% Decomposition.
15 min.	0.0332	0.03274	98.67
30 min.	0.0504	0.04999	99.25
60 min.	0.0354	0.0358	101.29
120 min.	0.0660	0.06531	99.01

TABLE 2.

3.6% Sodium Peroxide in 20% Alcohol.

Time	Gm. Chloropicrin taken	Gm. Chloropicrin found	% Decomposition.	Capacity of bottle in c.c.
1½ hour	0.0160	0.01607	100.43	500
1½ "	0.0151	0.0151	100.2	500
2 "	0.0380	0.03807	100.18	500
2 "	0.0282	0.0280	99.6	500
Overnight	0.0343	0.03423	99.81	2500
	0.0530	0.05296	99.92	2500
	0.0451	0.04509	100.0	2500
	0.0282	0.0283	100.68	2500

The Vacuum Bottle method gave results that were in accordance with those obtained by the Direct Method. Samples of chloropicrin were weighed in sealed glass bulbs and were placed in 2½-liter bottles. Each bottle was evacuated and

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the bulb broken by shaking the bottle. 50 c.c. of the sodium peroxide solution were drawn in and the bottles were shaken for one-half hour and allowed to stand over night. The Sodium Peroxide Method of analysis was used. The purity of the sample used was 98.05%.

TABLE 3.

3.6% Sodium Peroxide in 50% Alcohol.

Gm. chloropicrin taken	Gm. Chloropicrin found	% Decomp.	Gm. Chloropicrin per Liter	Parts per million by Vol.	Conc. taken	Conc. found
0.0628	0.0630	100.4	0.0251	3,400	1/292	1/291
0.0787	0.0784	99.7	0.0314	4,285	1/233	1/234
0.0758	0.07643	100.8	0.0303	4,127	1/242	1/240
0.0502	0.0508	101.3	0.0200	2,733	1/365	1/361
0.1310[#]	0.1311	100.0	0.0524	7,140	1/140	1/140

[#] Capacity of bottle 4.4 liters.

Decomposition of Chloropicrin with Aqueous Solutions of Sodium Peroxide.

Strong solutions of the aqueous sodium peroxide were first used. It was found that dilute solutions of sodium peroxide will completely decompose ordinary concentrations of chloropicrin.

A series of determinations were made, keeping the amount of chloropicrin used constant, as nearly as possible,

and varying the strength of sodium peroxide solution used. The Vacuum Bottle method was used for the decomposition of the chloropicrin. The bottles were shaken for ½ hour and allowed to stand overnight except where the ¼% solution was used. This solution was analyzed at once. 50 mgm. in a 2½-liter bottle is equivalent to 20 mgm. per liter or a concentration of 1 part in 370. The ¼% to 1% solutions of sodium peroxide will easily decompose the ordinary concentrations of chloropicrin. The highest concentration that has been obtained in the field is about 1 part in 800.

TABLE 4.

Varying concentrations of Sodium Peroxide on Chloropicrin.

Strength Na_2O_2 in %	Gm. Chloropicrin taken	Per Cent Decomposition
13	0.0478	99.91
	0.0533	99.32
10	0.0529	100.3
7.2	0.0623	99.72
5.6	0.0530	99.92
	0.0504	99.25
3.6	0.0585	99.8
1	0.0536	98.8
½	0.0720	98.29
¼	0.0534	99.44
	0.0498	99.5

The next study taken up was to determine the strength of sodium peroxide solution necessary for the complete decomposition of various amounts and concentrations of chloropicrin. The limit of each concentration of sodium peroxide was obtained by taking a large sample and obtaining the decomposition value. If the result was low, the weight of chloropicrin was gradually decreased until complete decomposition was obtained. This gave the maximum concentration of chloropicrin that could be determined with a given sodium peroxide solution.

The following procedure was used throughout this work: The chloropicrin is weighed in glass bulbs, placed in 2½-liter bottles, the bottles evacuated, bulbs broken, and 50 cubic centimeters of freshly prepared sodium peroxide solution are drawn in. The bottles are each thoroughly shaken for the length of time indicated, and the contents immediately transferred to Erlenmeyer flasks. The solution is acidified with 5 cubic centimeters of concentrated nitric acid and excess of N/10 silver nitrate is added. The silver chloride is coagulated by boiling, if necessary, filtered off and washed. Two cubic centimeters of ferric alum indicator are added and the excess silver nitrate is titrated with N/10 sodium thiocyanate. A blank determination is carried out at the same time.

TABLE 5.

1/8% Solution of Sodium Peroxide on Chloropicrin
Time of Shaking - 1/2 hour

Cap. of Bottle	Chloropicrin Taken				Chloropicrin Found				
	Mgm.	Mgm. per liter	P.P.M. by vol.	Conc.	Mgm.	Mgm. per liter	P.P.M. by vol.	Conc.	% Decomp.
2560	24.2	9.4	1278	1/783	24.3	9.4	1278	1/783	100.3
2560	23.1	9.0	1223	1/817	23.3	9.1	1238	1/807	100.9
2560	34.8	13.6	1849	1/541	30.5	11.9	1620	1/617	87.7

Concentrations of chloropicrin as high as 1 part in 800, or 9 milligrams per liter are decomposed when shaken with 50 cubic centimeters of 1/8% sodium peroxide for 1/2 hour.

TABLE 6.

1/4% Solution of Sodium Peroxide on Chloropicrin
Time of Shaking - 1/2 hour

	Chloropicrin Taken				Chloropicrin Found				
Cap. of Bottle	Mgm.	Mgm. per liter	P.P.M. by vol.	Conc.	Mgm.	Mgm. per liter	P.P.M. by vol.	Conc.	% Decomp.
2540	91.8	36.15	4916	1-203	74.8	29.4	3998	1-250	81.48
2540	73.9	29.1	3958	1-253	64.3	25.3	3441	1-296	87.01
2540	68.5	29.6	3658	1-273	61.0	24.0	3264	1-306	89.05
2560	61.4	23.9	3250	1-308	58.8	22.9	3114	1-321	95.7
2560	60.8	23.8	2337	1-310	58.2	22.7	3087	1-324	95.7
2540	60.9	24.0	3264	1-306	60.1	23.6	3209	1-311	98.7
2540	58.6	23.7	3223	1-310	56.6	22.2	2019	1-331	96.5
2560	56.2	22.0	2987	1-334	54.9	21.4	2918	1-343	97.6
2560	56.1	21.9	2978	1-336	55.3	21.6	2938	1-341	98.75
2540	53.4	21.0	2856	1-350	53.1	20.9	2842	1-352	99.44
2560	49.8	19.4	2638	1-379	49.6	19.3	2625	1-382	99.5

A concentration of chloropicrin of one part in 375 or 19.6 milligrams per liter is decomposed by shaking 1/2 hour with 1/4% solution of sodium peroxide.

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

TABLE 7.

1/4% Solution of Sodium Peroxide on Chloropicrin
Time of Shaking - 1 hour

Cap. of Bottle	Chloropicrin Taken				Chloropicrin Found				
	Mgm.	Mgm. per liter	P.P.M. by vol.	Conc.	Mgm.	Mgm. per liter	P.P.M. by vol.	Conc.	% Decomp.
2540	89.7	35.4	4858	1-206	74.9	29.4	3998	1-250	83.5
2540	75.3	29.7	4039	1-248	70.8	27.8	3781	1-264	94.0
2540	70.2	27.6	3753	1-266	67.7	26.6	3618	1-276	96.5
2540	67.1	26.4	3590	1-278	66.6	26.2	3563	1-280	99.25

Increasing the time of shaking from 1/2 hour to 1 hour increases the amouht of chloropicrin decomposed. The amount of chloropicrin decomposed is not proportional to the increase in time. A concentration of 1 part in 280 or 26.2 milligrams per liter is completely decomposed by shaking for 1 hour with 1/4% solution of sodium peroxide.

TABLE 8.

1/2% Solution of Sodium Peroxide on Chloropicrin
Time of Shaking - 1/2 hour.

	Chloropicrin Taken				Chloropicrin Found				
Cap. of Bottle	Mgm.	Mgm. per liter	P.P.M. by vol.	Conc.	Gm.	Mgm. per liter	P.P.M. by vol.	Conc.	% Decomp.
2540	158.0	63.3	8465	1-118	148.1	58.4	7942	1-126	93.7
2540	145.5	57.2	7779	1-128	139.0	54.7	7439	1-134	95.5
2540	137.5	54.1	7358	1-136	130.4	51.3	6968	1-143	95.0
2540	124.0	49.2	6691	1-150	121.7	48.0	6528	1-153	97.5
2540	124.2	48.9	6650	1-150	121.9	48.0	6528	1-153	98.0
2540	119.9	47.2	6419	1-156	118.2	46.5	6324	1-157	98.7
2540	118.7	46.6	6338	1-158	116.1	45.7	6215	1-161	98.0

A concentration of chloropicrin of 1 part in 160 or 46 milligrams per liter is decomposed when shaken 1/2 hour with 1/2% solution of sodium peroxide.

The vapor pressure of chloropicrin at 30° C. is 30.5 mm. The highest concentration in air that can be obtained at this temperature is approximately 1 part in 50. The amount of sodium peroxide necessary to decompose this amount of chloropicrin was then taken up. The bottles were shaken for 1/2 hour and the analysis was completed at once. Decomposition was only complete with a 10% solution of sodium peroxide.

It will be noted on the table that a 1½% solution gave the same decomposition as a 5% solution with this procedure. No odor of chloropicrin could be detected nor was there any effect on the eye after shaking 1/2 hour, but on acidifying the odor of chloropicrin was very marked. When the bottles were shaken for 1/2 hour and allowed to stand over night, decomposition was complete with a 5% solution of sodium peroxide.

TABLE 9.

DECOMPOSITION OF CHLOROPICRIN
1 PART IN 50 WITH SODIUM PEROXIDE.

50 c.c. Aqueous Sodium Peroxide, Time of Shaking - Varied.

			Chloropicrin Taken				Chloropicrin Found		
Capty. of Bottle	Time Shaking	% Na_2O_2	Gm.	Mgm. per Liter	P.P.M. by Vol.	Conc.	Gm.	Conc.	De-comp.
2500	½ hr.	1½	0.3628	145.1	19734	1-50.6	0.3497	1-52.5	96.4
2566	½ "	"	0.3594	140.0	19040	1-52.5	0.3485	1-54.1	96.97
2566	½ "	"	0.3593	140.0	19040	1-52.5	0.3462	1-54.5	96.36
2566	½ "	1.6	0.3600	140.3	19080	1-52.4	0.3467	1-54.4	96.31
2566	½"	2.0	0.3657	142.5	19380	1-51.6	0.3513	1-53.7	96.07
2500	½ "	5.0	0.3613	144.5	19652	1-50.9	0.3491	1-52.6	96.6
2500	½"	0.75	0.3656	146.2	19883	1-50.3	0.3525	1-52.1	96.4
2546	3 hrs. on wheel	1.0	0.3658	143.6	19530	1-51.2	0.3541	1-52.8	96.8
2500	"	2.0	0.3657	146.3	19897	1-50.3	0.3515	1-52.3	96.1
2566	"	5.0	0.3670	143.0	19448	1-51.4	0.3571	1-52.8	97.3
2500	½ hr.	10.0	0.3627	145.1	19734	1-50.7	0.3561	1-51.6	98.2
2566	½hr. on wheel stood over-night	10.0	0.3789	147.6	20074	1-49.8	0.3753	1-50.2	99.04
2500	"	5.0	0.3669	146.8	19965	1-50.1	0.3619	1-50.8	98.90
2546	"	2.0	0.3637	142.8	19421	1-51.5	0.3490	1-53.6	95.95
2566	"	2.0	0.3629	141.4	19230	1-52	0.3503	1-53.8	96.50
2546	"	3.0	0.3671	144.2	19611	1-51	0.3575	1-52.4	97.40
2500	"	4.0	0.3651	146.0	19856	1-50.3	0.3577	1-51.4	97.98

The standard sodium peroxide method as outlined was given to a number of observers previously unacquainted with the method. The concentrations of peroxide used, as well as the concentrations of chloropicrin were varied. The results (Table 10) show that the method is relatively easy to manipulate and very accurate. The chloropicrin was weighed out in sealed glass bulbs and the Vacuum Bottle Method of decomposition was used.

TABLE 10.

DETERMINATION OF CHLOROPICRIN BY STANDARD SODIUM PEROXIDE METHOD BY DIFFERENT OBSERVERS.

50 c.c. of 13% Sodium Peroxide Absorbing Solution.
Time of Shaking - 15 Minutes.

Ob-servers	Chloropicrin Gms. Taken	Chloropicrin Gms. Found	Per-cent Decom-position	Mgm. per Liter	P.P.M. by vol.	Vol. of air cont. 1 vol. of gas Taken	Vol. of air cont. 1 vol. of gas Found	Time of stand-ing.
								EXCESSIVE SHAKING
4	0.0533	0.0529	99.32	101.5	13808	72	71	15 min.
4	0.0451	0.0451	100.00	85.9	11683	85	85	30 "
4	0.0297	0.0298	100.40	56.5	7693	130	129	1 hour
4	0.0508	0.0507	99.89	96.7	13160	76	76	1 "
4	0.0291	0.0290	99.89	55.4	7537	132	132	1½ "
4	0.0319	0.03189	99.98	60.7	8262	121	121	1½ "
6	0.0141	0.01413	100.23	5.5	751	1329	1327	Overnight
6	0.0478	0.0477	99.91	18.7	2549	392	592	"

50 c.c. of 10% Sodium Peroxide absorbing solution.
Time Shaken - 15 Minutes.

Ob-servers	Chloropicrin Gms. Taken	Chloropicrin Gms. Found	Per-cent Decom-position	Mgm. per Liter	P.P.M. by vol.	Vol. of air cont. 1 vol. of gas Taken	Vol. of air cont. 1 vol. of gas Found	Time of stand-ing.
4	0.0388	0.0383	98.85	73.9	10050	99	100	1 hour
4	0.0164	0.0163	99.77	31.2	4247	235	236	1 "
4	0.0529	0.0530	100.30	100.8	13710	72	72	1½ "
4	0.0640	0.0643	100.60	121.9	16580	60	59	" "

50 c.c. of 7.2% Sodium Peroxide Absorbing Solution.
Time Shaken - 15 Minutes.

Ob-servers	Chloropicrin Gms. Taken	Chloropicrin Gms. Found	Per-cent Decom-position	Mgm. per Liter	P.P.M. by vol.	Vol. of air cont. 1 vol. of gas Taken	Vol. of air cont. 1 vol. of gas Found	Time of stand-ing.
9	0.06585	0.06471	98.29	131.7	17910	55	56	1 hour
9	0.0623	0.0621	99.72	124.6	16940	59	59	1 "
9	0.03245	0.0323	99.63	64.8	8824	115	113	1½ "

TABLE 10 (continued)

50 c.c. of 5.6% Sodium Peroxide Absorbing Solution.

Time Shaken - No. 3 - 30 Minutes.
- No. 10- 15 Minutes.

Observers	Chloropicrin		Percent Decomposition	Mgm. per Liter	P.P.M. by vol.	Vol. of Air cont. 1 vol. of gas		Time of standing
	Gms. Taken	Gms. Found				Taken	Found	
3								
3	0.016	0.01606	100.43	32.0	4352	229	228	1½ hr.
3	0.038	0.03806	100.18	19.0	2584	387	386	2 "
3	0.0343	0.0342	99.81	13.72	1865	535	536	Overnight
3	0.0530	0.0529	99.92	21.20	2883	346	347	"
3	0.0451	0.0451	100.00	18.04	2453	407	407	"
3	0.0282	0.02839	100.68	11.28	1534	651	647	"
3	0.0151	0.01507	99.82	30.2	4107	243	243	1½ hr.
3	0.0282	0.02808	99.60	56.4	7670	130	130	2 "
10	0.0660	0.0654	99.01	26.1	3560	281	278	2 "
10	0.0504	0.0500	99.25	20.0	2725	367	364	½ "
10	0.0402	0.04085	101.7	16.3	2225	450	456	1 "

50 c.c. of 1.5% Sodium Peroxide Absorbing Solution.

Time Shaken - 30 Minutes.

7	0.0230	0.02317	100.6	9.08	1235	809	804	Overnight
7	0.0071	0.00712	100.1	2.74	373	2681	2678	"
7	0.00968	0.00959	99.1	3.8	517	1934	1951	"
7	0.00554	0.00550	99.3	2.3	313	3195	3218	"
7	0.00998	0.00991	99.3	3.5	476	2101	2115	"
7	0.0155	0.0155	100.0	6.0	816	1225	1225	"

50 c.c. of 1.5% Sodium Peroxide Absorbing Solution.

Time Shaken - 30 Minutes.

7	0.00939	0.00933	99.4	3.9	530	1887	1898	Overnight
7	0.00875	0.00869	99.3	3.4	462	2164	2179	"
7	0.00781	0.00776	99.4	3.3	449	2299	2313	"

50 c.c of 1% Sodium Peroxide Absorbing Solution.

Time Shaken - 30 Minutes.

2	0.03163	0.0316	99.9	12.7	1727	578	579	12 hrs.
2	0.0761	0.0769	101.0	29.5	4012	249	246	" "

TABLE 10 (Concluded)

50 c.c. of 1.5% Sodium Peroxide Absorbing Solution.
Time Shaken - 30 Minutes.

Observers	Chloropicrin		Per cent Decomposition	Mgm. per Liter	P.P.M. by vol.	Vol. of Air cont. 1 vol. of gas		Time of standing.
	Gms. Taken	Gms. Found				Taken	Found	
11	0.0202	0.0201	99.2	7.91	1076	928	935	Overnight
11	0.0330	0.0329	99.8	12.82	1743	573	574	"
11	0.0219	0.0218	99.3	8.43	1146	872	878	"
11	0.0259	0.0257	99.1	10.00	1360	735	741	"
11	0.0197	0.0195	99.0	7.59	1032	968	977	"
50 c.c. of 0.5% Sodium Peroxide Absorbing Solution. Time Shaken - 30 Minutes.								
5	0.0294	0.0292	99.09	11.60	1576	634	640	
5	0.0421	0.0415	98.7	16.2	2211	452	457	
50 c.c. of 3.6% Sodium Peroxide Absorbing Solution Time Shaken - 15 Minutes.								
1	0.0979	0.0978	99.90	39.12	5337	187	188	Overnight
1	0.1120	0.1118	99.60	44.72	6106	164	165	"
1	0.0585	0.0583	99.80	23.52	3199	312	315	"
1	0.0753	0.0752	99.80	30.08	4105	244	244	"
1	0.0326	0.0328	100.5	13.12	1777	565	560	"
1	0.0316	0.0318	100.75	12.72	1722	582	578	"

The standard sodium peroxide method was then given to five observers who were acquainted with the method. They were given unknown weights of chloropicrin in sealed glass bulbs. They used the Vacuum Bottle method of decomposition.

50 c.c. of 1/2% sodium peroxide solution were used in each case and the bottles were shaken for 1/2 hour, and allowed to stand for two hours before proceeding with the analysis. Blank determinations were made by each man. The results were satisfactory and again showed that the method was accurate. (Table 11).

TABLE 11.

DETERMINATION OF UNKNOWN CONCENTRATIONS OF CHLOROPICRIN WITH SODIUM PEROXIDE BY DIFFERENT OBSERVERS.

50 c.c. of 0.5% Sodium Peroxide Absorbing Solution.
Time Shaken - 30 Minutes.

Observers	Chloropicrin		Percent Decomposition	Mgm. per Liter	P.P.M. by vol.	Vol. of Air cont. 1 vol. of gas		Time of standing.
	Gms. Taken	Gms. Found				Taken	Found	
1	0.0061	0.0060	99.2	2.42	329	3014	3035	2 hr.
2	0.0148	0.0146	99.7	5.93	805	1250	1265	"
3	0.0132	0.0126	97.6	5.25	715	1420	1470	"
4	0.0300	0.0297	100.06	12.00	1632	620	620	"
5	0.0417	0.0405	98.04	16.67	2268	444	450	"

ACTION OF SODIUM SULPHITE ON CHLOROPICRIN.

Chloropicrin is quantitatively decomposed when acted upon by sodium sulphite.[1] Two chlorine atoms in the chloropicrin are replaced by sulphonic acid groups, and the third chlorine is substituted by hydrogen by virtue of the reducing action of the sulphurous acid. The reaction may be written as follows:

$$C\ (No_2)\ Cl_3 + 3\ Na_2So_3 + H_2O = CH(No_2)(So_3Na)_2 + 3NaCl - NaHSo_4$$

The maximum concentration of chloropicrin completely decomposed by a 3% sodium sulphite solution in 30% alcohol was studied. The chloropicrin was weighed in sealed glass bulbs and the Standard Sodium Sulphite method was used with the Vacuum Bottle Method. The bottles were thoroughly shaken for 1/2 hour and the contents immediately transferred to an Erlenmeyer flask and analysed. The decomposition of chloropicrin would be higher for the larger amounts of chloropicrin given in the table, if the absorbent had remained in contact with it a longer time, for example, over night. A concentration of 147 milligrams per liter of chloropicrin is completely decomposed by the alcoholic sodium sulphite solution when shaken for 1/2 hour.

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[1] J. Chem. Soc. 25, 389.
Jahr. der Chem. (1872) 578.
Chem. Centr. (1870), 770.
Chem. Centr. (1872), 638.

TABLE 12.

Action of Alcoholic Sodium Sulphite on Chloropicrin.

TAKEN				FOUND				
Gms. Chloro-picrin	Mgm. per Liter	P.P.M. by vol.	Conc.	Gms. Chloro-picrin	Mgm. per Liter	P.P.M. by vol.	Conc.	% De-comp.
0.3637	142.8	19,420	1-51.5	0.3575	140.4	18,994	1-52.6	98.31
0.3781	151.2	20.568	1-48.6	0.3699	146.8	19,959	1-50.1	97.83
0.3835	150.6	20,481	1-48.8	0.3770	148.1	20,141	1-49.6	98.31
0.3869	151.9	20,658	1-48.4	0.3814	149.8	20,372	1-49.1	98.58
0.4393	172.5	23,460	1-42.6	0.4147	162.9	22,154	1-45.1	94.41
0.4412#	173.3	23,568	1-42.~~2~~4	0.3550	139.4	18,958	1-52.8	80.47
0.4446	174.6	23,745	1-42.5	0.3522	138.3	18,808	1-53.2	79.23
0.5196	204.1	27,754	1-36.0	0.3691	144.9	19,706	1-50.7	71.64
0.5233#	209.3	28,467	1-35.1	0.4042	161.7	$\overset{2}{3}$1,988	1-45.5	77.24
0.8073	322.9	43,914	1-22.8	0.3982	159.3	$\overset{2}{3}$1,622	1-46.2	49.33

#Gas remained in contact with the absorbing solution from 2 - 3 hours before shaking. It was then shaken ½ hour.

Comparison of Sodium Peroxide and Sodium Sulphite Methods.

A comparison study of the aqueous sodium peroxide and alcoholic sodium sulphite methods for the analysis of chloropicrin was carried out to determine how the two methods compare when one is used as a check upon the other. The use of the alcoholic sodium sulphite solution makes it necessary to boil off the alcohol and sulphur dioxide. This part of the procedure consumes considerable time. In using the sodium peroxide method one may proceed at once with the analysis. The methods were compared by collecting duplicate samples in a gas chamber. (See Photograph No. 6). The two open ends of a glass T (sealed at one end) were inserted into the rubber tubing of two evacuated bottles. The screw clamp on the rubber tubing was released, and by breaking the sealed glass tip a duplicate sample was taken through a common orifice. After taking the sample the clamp on the rubber tubing was immediately tightened. In this manner each pair of bottles contained the same sample of gas.

A high concentration of chloropicrin was produced by atomizing liquid chloropicrin in an air tight chamber 16' x 16' x 12'. After the liquid was atomized, fifteen minutes were allowed for the gas to become diffused in the chamber. Eight duplicate samples of gas were collected from different parts of the chamber. Samples No. 1 and 11 were taken on a shelf four feet from the floor, while the remaining samples were taken near the floor.

50 cubic centimeters of a 1% aqueous solution of sodium peroxide were introduced into one bottle of each pair by means of the "L.P.G." Filler. (See Photograph No. 7 and No. 8.) Into the other bottle of each pair 50 c.c. of 3% sodium sulphite solution in 30% alcohol was introduced. The tubing clamps were again tightened and the bottles were shaken for 1/2 hour and allowed to stand over night before proceeding with the analysis.

TABLE 13.

COMPARISON OF AQUEOUS SODIUM PEROXIDE AND ALCOHOLIC SODIUM SULPHITE ON CHLOROPICRIN.

Pair No.	Absorbing Sol.	Wt. Chloropicrin	Pressure MM.	Cap. of Bottle Corr.	Mgm. per Liter	P.P.M. by vol.	Conc.	Mgm. per L. with $\frac{Na_2O_2}{Na_2SO_3}$
I	Na_2O_2	7.14	18	2524	2.82	383	1-2600	98.6%
	Na_2SO_3	7.25	15	2534	2.86	389	1-2565	"
II	Na_2O_2	8.60	18	2487	3.46	470	1-2125	98.6%
	Na_2SO_3	8.77	16	2598	3.51	477	1-2095	"
III	Na_2O_2	22.30	18	2476	9.00	1224	1-816	104.8%
	Na_2SO_3	20.93	22	2440	8.58	1166	1-857	"
IV	Na_2O_2	23.56	18	2563	9.19	1249	1-800	98.0%
	Na_2SO_3	23.78	19	2535	9.38	1275	1-784	"
V	Na_2O_2	24.71	21	2528	9.77	1328	1-753	100.5%
	Na_2SO_3	24.41	16	2511	9.72	1321	1-756	"
VI	Na_2O_2	24.33	17	2511	9.69	1317	1-759	102.3%
	Na_2SO_3	24.00	18	2534	9.47	1288	1-776	"
VII	Na_2O_2	23.51	17	2454	9.58	1302	1-767	95.1%
	Na_2SO_3	24.70	18	2452	10.07	1369	1-730	"
VIII	Na_2O_2	26.41	19	2514	10.51	1429	1-699	103.1%
	Na_2SO_3	25.64	17	2515	10.19	1385	1-728	"
							Average -----	100.1%

From the results obtained in the above table, it was deemed advisable to use the sodium peroxide method for the determination of all field concentrations. The alcoholic sodium sulphite method is too slow and requires care in boiling. In the sodium peroxide method no heat is necessary except to coagulate the precipitate of silver chloride.

Comparison of the Volhard and Mohr Methods of Titration in Sodium Peroxide Method.

The substitution of the Mohr titration method for chlorides instead of the Volhard method would shorten the procedure still more in the aqueous sodium peroxide method. The low concentration of sodium peroxide used made it desirable to compare the two methods.

The Vacuum Bottle method was used and 50 cubic centimeters of 1½% aqueous sodium peroxide were introduced as the absorbent. The bottles were shaken on the shaking wheel for ½ hour. The contents of the bottles were then made up to a definite volume with water in a volumetric flask, and aliquot portions were taken for analysis by the two methods. Both titrations were made in Erlenmeyer flasks against a white background, when the chloride content was high enough so that N/10 silver nitrate could be used. When N/100 silver nitrate was used, the titrations were made in a casserole.

The Volhard method used in this comparison was the same as described in the Standard Sodium Peroxide Method.

The Mohr method was used as follows: The aliquot sample was transferred either to an Erlenmeyer Flask or a

porcelain casserole, and diluted to 50 - 75 cubic centimeters. A few drops of phenolphtholein solution were added, and the alkalinity carefully neutralized with N/1 nitric acid. 1 c.c. of potassium chromate indicator was added, and standard silver nitrate carefully run in from a burette until the first faint red color of silver chromate appeared. A blank reading obtained by titrating distilled water containing the same amount of indicator was subtracted from the reading obtained above.

The weights of "Chloropicrin taken" are the amount of chloropicrin in the aliquot sample taken and the concentrations are calculated on the basis of the 2½-liter bottles used. A new sample of chloropicrin was taken in each determination, except in No. 6 and No. 7. In these two determinations, a larger aliquot was taken in Determination No. 6.

When the concentration of chloropicrin is high enough so that N/10 solutions of silver nitrate may be used (i.e., concentrations of 1 part in 1100 or higher) the Mohr method may be substituted for the Volhard method without loss in accuracy, but with a gain in speed. When N/100 silver nitrate solutions are used, the end point in both methods becomes less sharp, usually resulting in a slight overtitration. This produces somewhat higher results with the Mohr method and lower results in the Volhard method. Under ordinary lighting conditions the Volhard endpoint is considerably more delicate. For low concentration work the Volhard method is the more accurate and better method to use.

COMPARISON OF VOHLHARD AND MOHR TITRATION IN SODIUM PEROXIDE METHOD.

Method.	Chloropicrin Taken CONCENTRATION MGM.	Mgm.per Liter	p.P.M. by vol.	Vol.of air containing 1 vol.of gas	Chloropicrin Found CONCENTRATION MGM.	Mgm.per liter	P.P.M. by vol.	Vol. of air containing 1 vol.of gas	% Decomp.
Mohr#	32.4	12.96	1762	567	31.65	12.66	1721	550	97.7
Volhard#	32.4	12.96	1762	567	31.67	12.67	1723	500	97.7
Mohr#	16.51	6.60	897	1114	16.57	6.63	901	1109	99.8
Volhard#	16.51	6.60	897	1114	16.55	6.62	900	1110	99.7
Mohr	8.20	3.28	446	2241	8.51	3.40	462	2162	103.7
Volhard	8.20	3.28	446	2241	8.10	3.24	440	2269	98.4
Mohr	4.06	1.624	220	4527	4.21	1.68	228	4376	103.7
Volhard	4.06	1.624	220	4527	4.01	1.60	217	4595	98.7
Mohr	3.56	1.424	193	5163	3.43	1.37	186	5367	96.4
Volhard	3.56	1.424	193	5163	3.56	1.43	194	5141	100.5
Mohr	5.496	2.198	208	3345	5.42	2.168	294	3391	98.6
Volhard	5.496	2.198	208	3345	5.41	2.164	294	3307	98.4
Mohr	0.900	0.3602	48	20,412	0.9647	0.3859	52	19,055	107.1
Volhard	0.857	0.3429	46	21,445	0.8275	0.3310	45	22,212	96.5

Standard solutions used in these four trials were N/10, all others were N/100.

Sodium Amalgam Method for Determining Chloropicrin.

Sodium amalgam is a very convenient reducing agent to use due to the ease with which the reaction may be controlled. One of the most accurate methods worked out for determining the chlorine of chloropicrin is the reduction of chloropicrin with sodium amalgam in alcohol. The method has been applied as a Direct method, and on gas concentrations of chloropicrin in the Vacuum Bottle method.

The amalgam is prepared according to methods outlined by Gatterman[1] and Thorpe.[2]

Direct Method.

Samples from 0.050 to 0.200 grams of chloropicrin were weighed in a sealed glass bulb. 35 grams of finely ground sodium amalgam were placed in a 300 c.c. Erlenmeyer flask and 50 c.c. of 75% alcohol were added. After the first reaction was over, the bulb containing the chloropicrin was placed in the flask, and the bulb broken by striking it with a glass rod. Then the flask was tightly stoppered and allowed to stand overnight.

The mercury was filtered off and washed. The filtrate was boiled to remove the alcohol, cooled, and acidified with concentrated nitric acid using 2 c.c. in excess. An excess of N/10 silver nitrate was added and the solution was heated to coagulate the silver chloride. The precipitate was

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[1] Methods of Organic Chemistry. Gatterman, p. 352.
[2] Dictionary of Applied Chemistry. Thorpe. 5, 5.

filtered off, washed and the filtrate was titrated with N/10 sodium thiocyanate using 5 cubic centimeters of ferric alum as the indicator.

A blank determination was made under the same conditions as the procedure.

TABLE 15.

ACTION OF SODIUM AMALGAM ON CHLOROPICRIN.

Purity of Sample - 98.36%
35 grams of Sodium Amalgam in 50 c.c. of 75% Alcohol.

No.	Gm. Chloropicrin Taken	Gm. Chloropicrin Found	Percent Decomposition.
2	0.1418	0.1405	99.1
3	0.1465	0.1452	99.1
4	0.1456	0.1457	100.01
5	0.0717	0.0713	99.5
6	0.0740	0.0739	99.9
7	0.0554	0.0549	99.05
9	0.0879	0.0875	99.57
10	0.0629	0.0627	99.64
11	0.01301	0.1293	99.42
12	0.01005	0.0999	99.42
13	0.0994	0.0988	99.37

Vacuum Bottle Method.

The Vacuum Bottle Method was carried out as usual, except that the sodium amalgam was put into the bottle with the bulb of chloropicrin before evacuation. The quantitative results obtained were very satisfactory.

[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

TABLE 16.

ANALYSIS OF CHLOROPICRIN WITH SODIUM AMALGAM.

Purity of Sample - 98.36%
35 grams of Sodium Amalgam in 50 c.c. of 75% Alcohol.

Gms. chloropicrin Taken	Gms. chloropicrin Found	Chloropicrin per liter	Parts per Million by vol.	Concentration Taken	Concentration Found	Percent Decomposition	Capacity of bottle in Liters
0.1391	0.1389	0.0623	8,489	1/117.8	1/118	99.88	2.232
0.0936	0.0929	0.0373	5,082	1/196.8	1/198.2	99.22	2.505
0.0623	0.0621	0.0280	3,815	1/314	1/315.5	99.62	2.225
0.0708	0.0704	0.0326	4,442	1/225	1/227	99.38	2.175

The sodium amalgam method involved an extra filtration for removing the mercury. The results however, were so satisfactory that it should be used where accuracy and not speed are required. Blank determinations were made with each experiment but in every case there was no value obtained for the blank.

Action of Alcoholic and Aqueous Sodium Hydroxide on Chloropicrin.

Bassett[1] says that chloropicrin is not affected by dilute sodium hydroxide in water, but slowly in alcohol. Stenhouse,[2] however, found that aqueous solutions of caustic alkalies affect chloropicrin gradually and that potassium chloride and potassium nitrate crystals separate. It is difficult to explain

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[1] Bassett, J. Chem. Soc. 17, 198, (1864)
J. Chem. 1847, 539.

[2] Stenhouse, Chem. Centr. (1848) 586.

why a neutral salt like sodium sulphite completely decomposes chloropicrin while solutions of caustic alkalies have but little effect.

Due to the lack of definite data on this matter, the action of aqueous and alcoholic solutions of sodium hydroxide on chloropicrin was studied. In studying methods for the analysis of mixtures, it was necessary to know what effect any substance present would have. A 10% alcoholic sodium hydroxide solution gave a decomposition of about 67%, which is equivalent to two atoms of chlorine.

Aqueous solutions of sodium hydroxide under similar conditions gave a decomposition of 33% for 5% to 10% solutions of sodium hydroxide equivalent to about one atom of chlorine.

Alcoholic Sodium Hydroxide on Chloropicrin.

The Vacuum Bottle and Standard Sodium Hydroxide methods of analysis were used in this study. Sodium hydroxide solutions from ½% to 10% in 20% alcohol were used. The per cent decomposition increases,

(1) With the time of shaking,

(2) With the strength of solution used, and

(3) The decrease in the size of sample used.

Each bottle was shaken the indicated length of time on the shaking wheel and allowed to stand over night (16 hours). Blank determinations were made with each series of runs.

TABLE 17.

ACTION OF ALCOHOLIC SODIUM HYDROXIDE ON CHLOROPICRIN.

10% NaOH in 20% Ethyl Alcohol Solution - 50 c.c. Used.
Time Standing - Over Night.

Gram Chloropicrin Taken	Gram Chloropicrin Found	% De-Comp.	Mgm. per Liter	Conc. Taken	Conc. Found	P.P.M. Taken	Time of Shaking Min.	Capacity of Bottle
0.0298	0.0200	67.26	11.6	1/633	1/942	1577	5	2565
0.0166	0.0117	70.57	6.4	1/1148	1/1627	870	5	2568
0.0609	0.0456	75.02	23.7	1/310	1/412 3	3223	10	2563
0.0314	0.0213	67.83	12.2	1/602	1/888	1659	30	2563
0.0249	0.0171	68.69	9.7	1/819	1/1192	1220	30	2563
0.0287	0.0198	69.20	11.3	1/650	1/940	1536	30	2539
0.0214	0.0148	70.50	8.4	1/873	1/1238	1145	30	2539
0.0336	0.0253	76.61	13.1	1/561	1/733	1780	30	2565

5% NaOH in 20% Ethyl Alcohol Solution - 50 c.c. Used.
Time Standing - Over Night.

Gram Chloropicrin Taken	Gram Chloropicrin Found	% De-Comp.	Mgm. per Liter	Conc. Taken	Conc. Found	P.P.M. Taken	Time of Shaking Min.	Capacity of Bottle
0.0117	0.0061	52.12	4.6	1/1059	1/2033	626	10	2539
0.0219	0.0118	53.77	8.9	1/827	1/1538	1209	10	2563
0.0332	0.0165	49.70	12.9	1/566	1/1140	1764	15	2568
0.0204	0.0112	54.91	8.0	1/919	1/1673	1088	15	2535
0.0195	0.0112	51.50	7.7	1/956	1/1662	1045	30	2539
0.0144	0.00868	60.34	5.6	1/1310	1/2172	762	30	2563
0.0135	0.00815	60.42	5.3	1/1382	1/2287	723	30	2535
0.0153	0.00935	61.13	5.36, 6.95	1/1233	1/2018	810	30	2565
0.0174	0.0107	61.39	6.8	1/1086	1/1769	920	30	2568
0.0228	0.0149	65.53	8.9	1/828	1/1263	1207	30	2565
0.0238	0.0165	69.08	9.4	1/784	1/1135	1274	30	2539
0.0200	0.0131	65.76	7.8	1/943	1/1435	1059	45	2563
0.0131	0.0087	66.63	5.1	1/1441	1/2163	693	60	2568
0.0245	0.0177	72.32	5.55	1/769	1/1064	1298	90	2565

2% NaOH in 20% Ethyl Alcohol Solution - 50 c.c. used.
Time Standing - Over Night.

Gram Chloropicrin Taken	Gram Chloropicrin Found	% De-Comp.	Mgm. per Liter	Conc. Taken	Conc. Found	P.P.M. Taken	Time of Shaking Min.	Capacity of Bottle
0.0213	0.0103	48.45	8.3	1/892	1/1800	1120	10	2563
0.0220	0.0107	48.76	8.7	1/848	1/1739	1179	15	2565
0.0160	0.00787	49.19	6.2	1/1178	1/2395	848	15	2565
0.0203	0.0104	51.40	7.9	1/930	1/1810	1074	30	2568

TABLE 17 (Concluded)

1% NaOH in 20% Ethyl Alcohol Solution - 50 c.c. Used.
Time Standing - Over Night

Gram. Chloropicrin Taken	Found	% De-Comp.	Mgm. per Liter	Conc. Taken	Conc. Found	P.P.M. Taken	Time of Shaking Min.	Capacity of Bottle
0.0157	0.00447	28.47	6.1	1/1201	1/4220	832	15	2563
0.0167	0.00513	30.71	6.51	1/1129	1/3677	885	15	2565
0.0166	0.00731	44.04	6.57	1/1119	1/2541	893	30	2477
0.0136	0.00607	44.62	5.3	1/1387	1/6108	720	30	2563
0.0215	0.00968	45.04	8.4	1/877	1/1948	1139	30	2563
0.0180	0.00961	53.40	7.02	1/1048	1/1964	953	30	2565
0.0116	0.00658	56.77	4.5	1/1630	1/2871	613	30	2571

½% NaOH in 20% Ethyl Alcohol Solution - 50 c.c. Used
Time Standing - Over Night

0.0269	0.00886	32.96	10.6	1/693	1/2104	1441	30	2539
0.0360	0.0120	33.40	14.2	1/512	1/1534	1931	30	2542
0.0252	0.00864	34.28	10.0	1/735	1/2144	1360	30	2508
0.0332	0.01164	35.07	13.4	1/548	1/1564	1822	30	2477
0.0184	0.00667	36.27	7.2	1/1020	1/2812	979	30	2563
0.0218	0.00806	36.98	8.6	1/854	1/2311	1169	30	2550
0.0171	0.00699	40.88	6.7	1/1097	1/2684	911	30	2563
0.0230	0.00969	42.13	8.95	1/821	1/1949	1217	30	2571
0.0242	0.01142	47.18	9.5	1/773	1/1642	1292	30	2535

B. Aqueous Sodium Hydroxide on Chloropicrin.

The Vacuum Bottle and Standard Sodium Hydroxide method were used with aqueous solutions of ½% to 10% sodium hydroxide. The shaking was done on the shaking wheel and every sample was shaken the same length of time. The decomposition increases with the strength of the sodium hydroxide solution used. The amount of decomposition increases as the

size of the sample taken decreases. This is affected by boiling, time of standing, slight solubility of chloropicrin in water, etc. Blank determinations were made simultaneously with the analysis.

TABLE 18.

ACTION OF AQUEOUS SODIUM HYDROXIDE ON CHLOROPICRIN.

No.	Gram Chloropicrin Taken	Gram Chloropicrin Found	Per cent Decomposition	Mgm. chloropicrin per liter	P.P.M. Taken	Concentration Taken	Concentration Found
10% NaOH Solution Used - Time of Shaking 30 Minutes Time of Standing 16 - 18 hours.							
1	0.0871	0.0203	23.55	34.84	4738	1/211	1/896
2	0.0443	0.0105	24.00	17.3	2352	1/425	1/1771
3	0.0731	0.0182	25.19	28.4	3862	1/258	1/1027
4	0.0368	0.00926	25.59	14.37	1954	1/511	1/1996
5	0.0267	0.00845	28.18	10.3	1400	1/713	1/2834
6	0.0245	0.0069	28.41	9.61	1306	1/756	1/2693
7	0.0205	0.00641	31.76	8.2	1115	1/896	1/2823
5% NaOH Solution Used - Time of Shaking 30 Minutes Time of Standing 16 - 18 Hours.							
1	0.0446	0.01085	24.58	17.84	2426	1/412	1/1676
2	0.0252	0.00789	31.57	9.84	1338	1/747	1/2366
3	0.0237	0.00743	31.73	9.48	1289	1/775	1/2444
4	0.0240	0.00756	31.80	9.37	1274	1/784	1/2467
5	0.0196	0.0069	35.51	7.69	1045	1/956	1/2692
2% NaOH Solution Used - Time of Shaking 30 Minutes Time of Standing 16 - 18 Hours.							
1	0.0370	0.00603	16.49	14.3	1944	1/514	1/3118
2	0.0170	0.00296	17.63	6.65	904	1/1105	1/6271
3	0.0177	0.00318	18.20	6.87	934	1/1089	1/5987
4	0.0364	0.00663	18.45	14.16	1825	1/547	1/2968
5	0.0273	0.00543	20.06	10.9	1482	1/674	1/3362

TABLE 18 (concluded)

No.	Gram Chloropicrin Taken	Gram Chloropicrin Found	Per cent Decomposition	Mgm. chloropicrin per liter	P.P.M. Taken	Concentration Taken	Concentration Found
1% NaOH Solution Used - Time of Shaking 30 Minutes Time of Standing 16 - 18 Hours.							
1	0.0424	0.00304	7.17	16.96	2306	1/433	1/6046
2	0.0192	0.00154	8.02	7.68	1044	1.957	1/10690
3	0.0215	0.00186	8.65	8.4	1142	1/875	1/10120
4	0.0281	0.00271	9.64	10.9	1482	1/674	1/7000
5	0.0144	0.00198	13.75	5.65	768	1/1301	1/9464
1½% NaOH Solution Used - Time of Shaking 30 Minutes Time of Standing 16 - 18 Hours.							
1	0.0615	0.00228	3.72	23.9	3250	1/307	1/8268
2	0.0187	0.00105	5.64	7.2	979	1/1021	1/18106
3	0.0245	0.00143	5.86	9.6	1305	1/765	1/13071
4	0.0134	0.000886	6.61	5.3	720	1/1387	1/20987
5	0.0105	0.000774	7.37	4.1	557	1/1793	1/24333
1/2% NaOH Solution Used - Time of Shaking 30 Minutes Time of Standing 140 Hours							
1	0.0595	0.0052	8.74	23.3	3168	1/315	1/3610
2	0.0212	0.00201	9.48	8.48	1153	1/867	1/9145
3	0.0222	0.00247	11.12	8.6	1169	1/855	1/7688
4	0.0140	0.00367	26.21	5.4	734	1/1362	1/5196

Action of Aqueous and Alcoholic Solutions of Sodium Carbonate on Chloropicrin.

It was important to know whether a solution of sodium carbonate, aqueous or alcoholic, had any effect on chloropicrin. If there were no action, a mixture of two gases, one of which is decomposed by sodium carbonate, could be analyzed by sodium carbonate. The fact that caustic alkalies

attack chloropicrin much more than the literature indicated made it desirable to have quantitative data on the action of sodium carbonate. The strength of the aqueous sodium carbonate solutions used varied from 0.5% to 15%, while the strength of the alcoholic sodium carbonate solutions used varied from 0.5% to 10%. The alcoholic sodium carbonate solutions contained 30% alcohol, and a 15% solution of sodium carbonate in 30% alcohol cannot be prepared. The 10% sodium carbonate solution in alcohol crystallized outsomewhat, and, after standing over night, a small amount of sodium carbonate also crystallized out of the 5% solution.

In the 0.5% to 5% aqueous solutions, the percentage decomposition is relatively small, but still sufficient to affect the results in the analysis of a mixture. The error in using a 0.5% and 1% aqueous carbonate solution would be less than 1%. For 2% to 5% solutions, the error would be over 3%.

In the alcoholic solutions the percent decomposition varies from 0.40% for 23 mgm. per liter in a 0.5% alcoholic solution to 2.75% for 5.6 mgm. per liter in a 2% alcoholic sodium carbonate solution. For 3.3 mgm. per liter of chloropicrin, the per cent decomposition is 5.5% with a 10% aqueous solution, while for 3.7 mgm. per liter of chloropicrin with a 10% alcoholic solution, the percent decomposition is 32.4%.

The 5% to 10% alcoholic solutions of sodium carbonate decompose about 35% of the chloropicrin and is equivalent to one atom of chlorine. The action of these solutions is the same as the aqueous sodium hydroxide on chloropicrin.

0.5% aqueous solution of sodium carbonate gives results within 1% when used to decompose another compound in the presence of chloropicrin. A 1% aqueous solution of sodium carbonate will give an error of 2%. Stronger solutions should not be used, and alcoholic solutions of sodium carbonate cannot be used for the determination of any substance in the presence of chloropicrin.

The standard sodium carbonate method was used in the 2½-liter Vacuum Bottle. Each bottle was shaken on the shaking wheel for 30 minutes and allowed to stand over night (16 hours) before proceeding with the analysis. A blank determination was made with each run. 12 bottles were shaken on the wheel at one time, thus giving comparable results with varying concentrations of chloropicrin as well as varying strengths of sodium carbonate solution used.

TABLE 19.

ACTION OF 10% ALCOHOLIC SOLUTION OF SODIUM CARBONATE ON CHLOROPICRIN.

Gm. Chloropicrin Taken	Gm. Chloropicrin Found	Percent Decomp.	Mgm. per Liter	P.P.M.	Conc. Taken	Conc. Found
0.07186	0.00973	13.50	27.8	3781	1/264	1/1956
0.0435	0.00938	21.6	16.8	2282	1/438	1/2028
0.0406	0.00911	22.4	16.6	2252	1/444	1/1982
0.0196	0.00648	32.6	7.7	1043	1/959	1/2914
0.0125	0.00512	41.9	4.9	681	1/1468	1/3503
0.0295	0.00603	20.44	11.2	1523	1/656	1/3211
0.0452	0.01031	22.85	17.7	2407	1/415	1/1817
0.0150	0.004306	28.71	6.0	816	1/1225	1/4268
0.0224	0.00697	31.11	8.7	1138	1/845	1/2716
0.0093	0.003017	32.44	3.7	503	1/1987	1/6125

TABLE 19 (concluded)
ACTION OF 5% ALCOHOLIC SOLUTION OF SODIUM CARBONATE ON CHLOROPICRIN.

Gm. Chloropicrin Taken	Gm. Chloropicrin Found	Percent Decomp.	Mgm. per Liter	P.P.M.	Conc. Taken	Conc. Found
0.0397	0.0131	32.8	15.4	2094	1/479	1/1460
0.0408	0.0135	32.9	16.4	2229	1/493	1/1498
0.0486	0.0158	34.5	19.1	2593	1/385	1/1116
0.0263	0.0121	45.9	10.2	1383	1/723	1/1575
0.0154	0.00925	59.9	5.97	820	1/1219	1/2035

ACTION OF 2% ALCOHOLIC SOLUTION OF SODIUM CARBONATE ON CHLOROPICRIN

0.0676	0.00430	6.36	26.20	3563	1/281	1/4418
0.0226	0.00317	11.09	9.23	1255	1/797	1/7187
0.0278	0.00251	11.41	10.81	1470	1/680	1/5960
0.0077	0.00131	17.99	3.04	413	1/2421	1/13452

ACTION OF 1% ALCOHOLIC SOLUTION OF SODIUM CARBONATE ON CHLOROPICRIN

0.0576	0.00305	5.28	22.34	3038	1/329	1/6231
0.0366	0.00257	7.03	14.68	1996	1/501	1/7126
0.0270	0.00215	7.97	10.46	1674	1/597	1/7478
0.0227	0.00210	9.22	9.25	1258	1/795	1/8622
0.0101	0.00182	18.05	3.90	530	1/1887	1/10454

ACTION OF 1/2% ALCOHOLIC SOLUTION OF SODIUM CARBONATE ON CHLOROPICRIN

0.0666	0.00451	6.77	26.0	3536	1/282	1/4177
0.0296	0.00348	11.75	11.4	1550	1/645	1/5489
0.0228	0.00308	13.51	8.9	1210	1/826	1/6115
0.0452	0.00654	14.47	18.1	2461	1/406	1/2890
0.0066	0.00125	18.94	2.6	353	1/2828	1/24931

TABLE 20.

ACTION OF 15% AQUEOUS SOLUTION OF SODIUM CARBONATE ON CHLOROPICRIN.

No.	Gram Chloropicrin Taken	Gram Chloropicrin Found	Per-cent Decomp.	Mgm. per Liter	P.P.M.	Conc. Taken	Conc. Found
1	0.0798	0.001162	1.45	31.5	4284	1/233	1/16096
2	0.0458	0.0007732	1.69	17.8	2420	1/413	1/24443
3	0.0131	0.0005581	4.26	5.1	693	1/1442	1/33850

ACTION OF 10% AQUEOUS SOLUTION OF SODIUM CARBONATE ON CHLOROPICRIN.

4	0.0468	0.000644	1.37	18.3	2488	1/401	1/29328
5	0.0167	0.0005754	3.44	6.5	884	1/1131	1/32883
6	0.0128	0.0005153	4.02	5.1	693	1/1442	1/24875
7	0.0084	0.0004594	5.47	3.3	448	1/2228	1/40733

ACTION OF 5% AQUEOUS SOLUTION OF SODIUM CARBONATE ON CHLOROPICRIN.

8	0.0318	0.0005238	1.65	12.7	1727	1/578	1/35085
9	0.0117	0.0002661	2.28	4.5	612	1/1634	1/71666
10	0.0177	0.0004413	2.49	6.9	938	1/1065	1/42795
11	0.0052	0.0001802	3.47	2.0	272	1/3676	1/105951

ACTION OF 2% AQUEOUS SOLUTION OF SODIUM CARBONATE ON CHLOROPICRIN.

26.	0.0524	0.0005606	1.07	20.96	2850	1/387	1/36215
27.	0.0209	0.0003887	1.86	8.16	1109	1/901	1/48440
28.	0.0171	0.0004745	2.77	6.6	897	1/1114	1/40220
29.	0.0141	0.0004887 3	2.75	5.6	761	1/1313	1/47745

ACTION OF 1% AQUEOUS SOLUTION OF SODIUM CARBONATE ON CHLOROPICRIN.

30.	0.0612	0.0005007	1.82	23.9	3250	1/307	1/37520
31.	0.0243	0.0003005	1.23	9.7	1319	1/761	1/61910
32.	0.0187	0.0002143	1.14	7.5	1020	1/980	1/86000
33.	0.0057	0.0001282	2.25	2.2	299	1/3342	1/148530

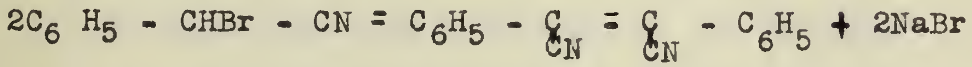
ACTION OF ½% AQUEOUS SOLUTION OF SODIUM CARBONATE ON CHLOROPICRIN.

34.	0.0713	0.003003	.42	23.3	3168	1/315	1/75143
35.	0.0448	0.0002148	.48	17.5	2380	1/420	1/87540
36.	0.0237	0.0001719	.72	9.6	1305	1/765	1/106370

BROMBENZYL CYANIDE.

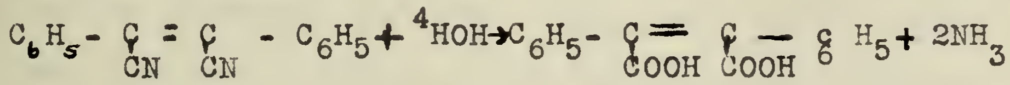
Pure Brombenzyl Cyanide is a white solid which melts at 25° - 27° C. On account of the difficulty in obtaining and preparing the crystals, brombenzyl cyanide is usually used in the solution of its mother liquor, and often contains some dibromide as impurity.

When brombenzyl cyanide is treated with an alcoholic solution of sodium hydroxide, dicyanstilbene is first formed as an intermediate product.[1]



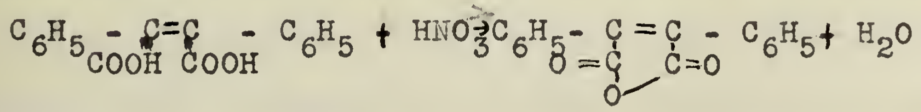
$$2C_6H_5 - CHBr - CN = C_6H_5 - \underset{CN}{C} = \underset{CN}{C} - C_6H_5 + 2NaBr$$

When samples of brombenzyl cyanide were shaken with a 50% alcoholic solution of sodium hydroxide, the solution was colored a deep greenish yellow, while a 10% alcoholic solution contained a precipitate. This compound was separated and crystallized from ether. The crystals were green and very soluble in ether and alcohol, and insoluble in water.



$$C_6H_5 - \underset{CN}{C} = \underset{CN}{C} - C_6H_5 + {}^4HOH \rightarrow C_6H_5 - \underset{COOH}{C} = \underset{COOH}{C} - C_6H_5 + 2NH_3$$

When the alcohol was evaporated off and the solution was acidified with concentrated nitric acid, a heavy flocculent yellow precipitate was formed, melting point 150° C.



$$C_6H_5 - \underset{COOH}{C} = \underset{COOH}{C} - C_6H_5 + HNO_3 \rightarrow C_6H_5 - C = C - C_6H_5 + H_2O$$

The formation of diphenyl maleic anhydride was avoided by adding a little sodium peroxide to the solution either at the beginning of the analysis or after the solutions

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[1] C. S. Reimer (Ber. 1797, (1881)

were transferred to the Erlenmeyer flasks.

The pure as well as the uncrystallized brombenzyl cyanide mother liquor was used in these experiments. When the solid was used, it was dissolved in alcohol and aliquots were used for analysis. Samples of the liquid were weighed out in sealed glass bulbs.

ANALYSIS WITH SODIUM HYDROXIDE SOLUTIONS.

10% sodium hydroxide in 10% alcohol

Halogen-free sodium hydroxide was prepared by dissolving metallic sodium in water.

In both the Direct and Vacuum Bottle method, 50 cubic centimeters of the sodium hydroxide solution were added to each bottle. The bottle was shaken for a few minutes and allowed to stand over night. The contents of the bottle were transferred to an Erlenmeyer flask and 15 cubic centimeters of 5% sodium peroxide (0.7 gms. Na_2O_2) were added, the alcohol was evaporated off, and the solution was acidified with 10 cubic centimeters of concentrated nitric acid. An excess of standard silver nitrate solution was added. The solution was boiled to coagulate the silver bromide, filtered, washed and cooled. The excess silver nitrate was titrated with standard sodium thiocyanate solution, using 2 - 3 cubic centimeters of ferric alum as the indicator. The solutions were made up to a volume of 150 cubic centimeters.

A blank determination was always made with the analysis.

SODIUM PEROXIDE METHOD.

In the Direct and Vacuum Bottle method, 50 c.c. of 3 - 5% aqueous sodium peroxide solution were added. The bottles were shaken and allowed to stand over night. After decomposition, the solution was warmed, if an alcoholic solution of brombenzyl cyanide was used. The solution was acidified with concentrated nitric acid and an excess of standard silver nitrate solution was added. The solution was boiled to coagulate the silver bromide, filtered, washed, and cooled. The excess silver nitrate was titrated with standard sodium thiocyanate using 2 - 3 c.c. of ferric alum as the indicator. A blank determination was made at the same time.

ANALYSIS WITH SODIUM ETHYLATE.

An absorbing solution containing 2 grams of sodium in 100 cubic centimeters of absolute alcohol was used. The weighed or aliquot sample and 25 c.c. of sodium ethylate were introduced into the bottles. The bottles were shaken at intervals for 1/2 hour and allowed to stand over night. After decomposition, the solutions were transferred to Erlenmeyer flasks. The alcohol was evaporated off and the solution was acidified with 10 c.c. of concentrated nitric acid. An excess of standard silver nitrate was added and the solution was boiled to coagulate the silver bromide, filtered off, washed, and cooled. The excess silver nitrate was titrated with standard sodium thiocyanate, using 2 - 3 c.c. of ferric alum as the indicator. The volume of the solution was about 150

c.c. for the titration. A blank determination was made to check the analysis.

EXPERIMENTAL.

5%, 10% and 15% solutions of sodium hydroxide in 50% alcohol were first used, but the 5% solution was unsatisfactory, whereas the 10% and 15% were equally good.

The vacuum bottle method was used, and 50 c.c. of absorbent were used in each case. The 50% alcoholic solutions were colored a deep greenish yellow, while the 10% and aqueous solutions were only slightly colored. After decomposition was complete, the solutions were transferred to Erlenmeyer flasks, the alcohol was evaporated off and acidified with nitric acid. A heavy flocculent yellow precipitate of diphenyl malcic anhydride was formed. An excess of standard silver nitrate was added and the solution was warmed to coagulate the silver bromide. Diphenylmaleic anhydride is quite soluble in hot water, and the solutions had to be well cooled before filtering. The precipitate had to be all filtered off as it gave the solution a yellow color that later interfered with the titration. The excess of silver nitrate was titrated with N/100 sodium thiocyanate, using 2 - 3 c.c. of ferric alum as indicator.

If the silver nitrate is added before filtering off the diphenylmaleic anhydride, the results are about 0.25% higher than when the diphenylmaleic anhydride is filtered off before. The purity of the sample used was 42.29% bromine.

TABLE 21.

ALCOHOLIC SODIUM HYDROXIDE ON BROMBENZYLCYANIDE

50 c.c. 10% NaOH in 50% Alcohol
Shaken five minutes and allowed to stand fifteen hours.

Gm. Brom-benzyl-cyanide Taken	Gm. Brom-benzyl-cyanide Found	% Decomp.	Capacity of Bottle in cc.	Mgm. Brom-benzyl-cyanide per liter	Parts per Million	Conc. Taken
0.0207	0.02054	99.24	2552	8.11	927	1/1079
0.01~~0~~96	0.01954	99.69	2590	7.56	865	1/1156
0.0193	0.01962	100.47	2556	7.55	863	1/1158
0.0190	0.01882	99.08	2552	7.44	851	1/1175
0.0211	0.02116	100.31	2556	8.25	943	1/1060
0.0125	0.01258	100.69	2552	4.89	559	1/1786
0.0196	0.01957	99.88	2552	7.68	877	1/1139

Reducing the amount of alcohol from 50% to 10% did not seem to effect the results, but the presence of 10% of alcohol was necessary to act as a solvent for the brombenzyl cyanide so that chemical reaction could take place more easily. (Table 22). A 10% aqueous solution of sodium hydroxide did not give complete decomposition.

TABLE 22.

ALCOHOLIC SODIUM HYDROXIDE ON BROMBENZYL CYANIDE

50 c.c. 10% NaOH in 10% Alcohol
Shaken five minutes and allowed to stand fifteen hours.

Gm. Brombenzylcyanide Taken	Gm. Brombenzylcyanide Found	% Decomp.	Capacity of Bottle in c.c.	Mgm. Brombenzylcyanide per liter	Parts per Million	Conc. Taken
0.0327	0.03223	98.58	2556	12.79	1462	1/684
0.0297	0.02973	100.09	2556	11.61	1148	1/870
0.0255	0.02553	100.12	2537	10.51	1099	1/910

The aqueous sodium hydroxide gave an average of 40.47% bromine or 95.69% decomposition (Table 23).

TABLE 23.

AQUEOUS SODIUM HYDROXIDE ON BROMBENZYLCYANIDE.

50 cc. 10% Aqueous NaOH. Shaken 5 min. & allowed to stand 15 hr.

Gm. Brombenzylcyanide Taken	Gm. Brombenzylcyanide Found	% Decomp.	Capacity of Bottle in cc.	Mgm. Brombenzylcyanide per liter	Parts per Million	Conc. Taken
0.0468	0.04503	96.22	2539	18.43	2106	1/475
0.0406	0.03881	95.60	2552	15.90	1818	1/550
0.0357	0.03398	95.18	2590	13.78	1575	1/635
0.0432	0.0$\overset{4}{5}$136	95.77	2552	16.92	1934	1/512

The results obtained using 10% alcoholic sodium hydroxide solution were quantitative but the method was

somewhat unsatisfactory, because of the time required and the difficulty in filtering off the diphenylmaleic anhydride. Small amounts of sodium peroxide solution were added to prevent the formation of the diphenylmalcic anhydride. Five cubic centimeters of 5% sodium peroxide solution (0.25 gram Na_2O_2) were added to each of four samples immediately after the sodium hydroxide solution (Table 24). Some diphenylmaleic anhydride was formed in each case when the decomposition solution was acidified with concentrated nitric acid.

TABLE 24.

SODIUM HYDROXIDE ON BROMBENZYLCYANIDE IN PRESENCE OF SODIUM PEROXIDE.

50 c.c. 10% NaOH in 10% Alcohol plus 5 cc. 5% Na_2O_2
Shaken five minutes and allowed to stand fifteen hrs.

Gm. Brom-benzyl-cyanide Taken	Gm. Brom-benzyl-cyanide Found	% De-comp.	Capa-city of bottle in cc.	Mgm.Brom-benzyl-cyanide per liter	Parts per Mil-lion by vol.	Conc. Taken
0.0270	0.02679	99.24	2539	10.63	1215	1/823
0.0144	0.01445	100.38	2552	5.64	644	1/1551
0.0275	0.02745	99.83	2590	10.61	1213	1/824
0.0251	0.02526	100.66	2552	9.83	1124	1/889

In the next experiment (Table 25) 10 c.c. of 5% sodium peroxide solution (0.5 gram Na_2O_2) was added to the decomposition solution after it was transferred from the bottle to an Erlenmeyer flask. This amount was sufficient to prevent

the formation of diphenylmalsic anhydride in all but the two larger samples of brombenzylcyanide taken.

TABLE 25.

SODIUM HYDROXIDE ON BROMBENZYL CYANIDE IN PRESENCE OF SODIUM PEROXIDE.

Gm. Brom-benzyl-cyanide Taken	Gm. Brom-benzyl-cyanide Found	% Decomp.	Capa-city of Bottle in cc.	Mgm. Brom-benzyl-cyanide per liter	Parts per Mill-ion by vol.	Conc. Taken
0.0145	0.01429	98.63	2556	5.67	648	1/1542
0.0178	0.01782	100.12	2552	6.97	797	1/1279
0.0322	0.03176	98.63	2557	12.59	1439	1/695
0.0280	0.02747	98.11	2537	11.03	1261	1/793

The above results show that brombenzylcyanide decomposed quantitatively by alcoholic sodium hydroxide. The best results were obtained by using a 10% solution of sodium hydroxide in 10% alcohol, to which 15 c.c. of 5% sodium peroxide solution (0.7 gm. Na_2O_2) was added, either at the same time that the sodium hydroxide was added or just before the solution was removed from the bottle (Table 26).

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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

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TABLE 26.

ALCOHOLIC SODIUM HYDROXIDE ON BROMBENZYLCYANIDE, IN PRESENCE OF SODIUM PEROXIDE.

50 c.c. 10% NaOH in 10% Alcohol. Shaken five minutes, allowed to stand fifteen hours, and 10 c.c. 5% Na_2O_2 added.

Gm. Brombenzylcyanide Taken	Gm. Brombenzylcyanide Found	% Decomp.	Capacity of Bottle in cc.	Mgm.Brombenzylcyanide per liter	Parts per Million by vol.	Conc. Taken
0.00327	0.00325	99.10	2556	1.28	146	1/6831
0.00250	0.00253	101.18	2552	0.98	112	1/8921
0.00205	0.00209	102.01	2557	0.80	92	1/10870
0.00172	0.00172	99.65	2537	0.67	77	1/12870

SODIUM PEROXIDE METHOD.

The use of small amounts of sodium peroxide in the alcoholic sodium hydroxide method of analysis of brombenzylcyanide suggested the use of aqueous sodium peroxide solutions alone. The Direct and Vacuum bottle method gave accurate results.

In the direct method, an alcoholic solution of brombenzyl cyanide was added to 50 c.c. of the aqueous solution of sodium peroxide in a 500 c.c. glass stoppered bottle. The bottle was shaken and allowed to stand over night. An ultimate analysis of the bromine content of this sample gave 42.32% (theoretical 40.78% Br.).

TABLE 27.

ACTION OF SODIUM PEROXIDE ON BROMBENZYLCYANIDE DIRECT METHOD.

Gm. Sample	Gm. Br_2 Found	% Br_2 Found	% Decomposition
	50 cc. 1% Sodium peroxide		
0.012	0.00456	38.20	90.27
0.012	0.00472	39.54	93.43
0.012	0.00463	38.80	91.44
	50 cc. 2% Sodium Peroxide		
0.012	0.00472	39.56	93.48
0.012	0.00478	40.08	94.71
	50 cc. 3% Sodium Peroxide		
0.012	0.00456	42.06	99.15
0.012	0.00493	41.76	98.44
0.012	0.00493	41.76	98.44
0.012	0.00499	42.24	99.55
	50 cc. 5% Sodium Peroxide		
0.012	0.00491	41.55	98.18
0.012	0.00515	43.66	103.17

The sample used in the Vacuum Bottle method contained 37.49% Bromine. An alcoholic solution of brombenzyl cyanide was first introduced into the evacuated bottle and then 50 c.c. of absorbing solution. The bottles were thoroughly shaken and allowed to stand over night.

TABLE 28.

DETERMINATION OF BROMBENZYLCYANIDE WITH SODIUM PEROXIDE.

50 c.c. 3% Sodium Peroxide

cc.01N $AgNO_3$	Gm. Sample	Gm.Br_2 Found	% Br_2 Found	Mgm.Per Liter	P.P.M.	% Decom.	Concen.
15.03	0.012410	.00462	37.22	4.964	567	99.28	1/1763
15.00	0.012410	.00449	36.20	4.964	567	99.65	1/1763
14.99	0.01404	.00528	37.63	5.616	641	100.30	1/1558
15.06	0.008846	.00332	37.49	3.538	404	100.16	1/2473
15.01	0.01371	.00553	37.43	5.484	626	99.84	1/1595

Action of Sodium Ethylate on Brombenzyl Cyanide.

The Direct method of analysis of brombenzyl cyanide was used with 5% sodium ethylate. 25 c.c. of sodium ethylate was added to a sample of brombenzyl cyanide in a glass stoppered bottle. The bottle was thoroughly shaken and allowed to stand over night. On standing, a yellow color formed which disappeared on the addition of nitric acid. The sample used contained 37.49% Bromine.

TABLE 29.

ACTION OF SODIUM ETHYLATE ON BROMBENZYL CYANIDE.

25 c.c. of 5% solution used.

Gm. of Sample	Gm. Br_2 Found	% Br_2 Found	% Decomposition
0.01805	0.006761	37.46	99.92
0,01805	0.006761	37.46	99.92
0.01805	0.006857	38.00	101.36
0.01805	0.006905	38.26	102.06

The Vacuum Bottle method was used with a 1% and 2% sodium ethylate solution. Both solutions decomposed brombenzyl cyanide quantitatively. 25 c.c. of the absorbing solution was used for each sample. The sample contained 37.49% bromine.

TABLE 30.

ANALYSIS OF BROMBENZYL CYANIDE WITH SODIUM ETHYLATE
25 c.c 2% Sodium Ethylate used.

Gm of Sample	CCN/100 $AgNO_3$ Used	Mgm.per liter	P.P.M. by vol.	Mgm. Br_2 Found	% Br_2 Found	% Decomp. Calc. on purity of Sample	Conc.
0.01371	6.37	5.484	626.84	5.0909	37.13	99.04	1/1595
0.01371	6.37	"	"	5.0909	37.13	99.04	"
0.01371	6.37	"	"	5.0909	37.13	99.04	"
0.01371	6.45	"	"	5.1548	37.60	100.29	"
0.01371	6.40	"	"	5.1149	37.31	99.52	"
0.01371	6.48	"	"	5.1788	37.77	100.75	"
25 c.c. 1% Sodium Ethylate.							
0.01521	7.11	6.0868	695.77	5.6823	37.35	99.63	1/1437
0.01521	7.10	"	"	5.6743	37.30	99.50	"
0.01521	7.08	"	"	5.6583	37.19	99.21	"
0.01521	7.06	"	"	5.6424	37.09	98.93	"
0.01521	7.00	"	"	5.5944	36.77	98.09	"

ACTION OF SODIUM SULPHITE ON BROMBENZYL CYANIDE.

The action of alcoholic sodium sulphite on brombenzyl cyanide was studied, the results obtained did not warrant any further work upon the problem. The Sodium Sulphite

solution did not decompose brombenzyl cyanide quantitatively. 7% and 9% solutions were tried but the results were not improved. A 9% solution of sodium sulphite in 30% of alcohol is a saturated solution. The per cent of bromine in the sample was 42.43%.

The Direct method of analysis with alcoholic sodium sulphite was used. Aliquot portions of an alcoholic solution of brombenzyl cyanide were used for analysis. The bottles were thoroughly shaken and allowed to stand over night before proceeding with the analysis.

TABLE 31.

ACTION OF ALCOHOLIC SODIUM SULPHITE ON BROMBENZYL CYANIDE
50 c.c. of 7% Sodium Sulphite

Gm. of Sample	Gm. of Br_2 Found	% Br. Found	% Decomp.
0.01083	0.00424	39.11	92.17
"	0.00398	36.70	86.50
"	0.00424	39.11	92.17

50 c.c. of 9% Sodium Sulphite

Gm. of Sample	Gm. of Br_2 Found	% Br. Found	% Decomp.
0.01083	0.00404	37.26	87.81
"	0.00409	37.85	89.21
0.01180	0.00452	38.25	90.15
"	0.00453	38.38	90.45
"	0.00451	38.18	89.17

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DICHLORDIETHYL SULPHIDE.

The solubility of dichlordiethyl sulphide (mustard gas) in water is about 0.1%. The dissolved dichlordiethyl sulphide is gradually hydrolyzed in the cold with the formation of hydrochloric acid, and more of the dichlordiethyl sulphide is dissolved. The rate of hydrolysis is increased on warming, and with hot water it is complete. The rate of hydrolysis in the cold is increased by the presence of dilute alkalies, such as sodium carbonate and sodium hydroxide and the neutral salt, sodium sulphite. In the cold, using aqueous solutions of sodium hydroxide and sodium carbonate, and alcoholic sodium sulphite, decomposition was not complete. Aqueous solutions of sodium peroxide and aqueous silver nitrate completely decompose dichlordiethyl sulphide. Sodium thiosulphate also gives complete decomposition.

The Standard sodium peroxide method was used in the Vacuum Bottle method of decomposition. Both high and low concentrations of dichlordiethyl sulphide were used. 50 c.c. of 2% aqueous sodium peroxide solution were used as the absorbing solution. The bottles were shaken continuously for one-half hour and allowed to stand over night. A blank determination was made along with the analysis. (Table 32).

TABLE 32.

DETERMINATION OF DICHLORDIETHYL SULPHIDE WITH SODIUM PEROXIDE METHOD.

50 c.c. 2% Aqueous Sodium Peroxide Solution
Shaking ½ hour. Standing over night.

Dichlordiethyl Sulphide			%	Parts			Capac-
Taken Gm.	Found Gm.	Mgm. per Liter	Decomposition	per Million	Conc. Taken	Conc. Found	ity of Bottle in cc.
0.0238	0.02381	9.38	100.06	1322	1/756.5	1/756.4	2535
0.0100	0.0100	3.87	100.06	545	1/1835	1/1835	2582
0.0277	0.02760	11.00	99.66	1551	1/643	1/647	2517
0.0114	0.01138	4.56	99.88	643	1/1555	1/1556	2500
0.0337	0.0334	13.24	98.96	1866	1/1336	1/541	2545
0.0132	0.0151	5.20	99.70	734	1/1362	1/1366	2535
0.0265	0.0262	10.6	98.98	1494	1/669	1/674	2500
0.0346	0.03452	13.74	99.79	1937	1/516	1/518	2517

The sodium peroxide method was used on as low concentrations of dichlordiethyl sulphide as may be volumetrically determined. A solution of dichlordiethyl sulphide in alcohol was used to measure out the small samples, and aliquot portions were introduced into 2½-liter evacuated bottles and determined according to the procedure.

TABLE 33.

DETERMINATION OF LOW CONCENTRATIONS OF DICHLORDIETHYL SULPHIDE WITH SODIUM PEROXIDE METHOD.

50 c.c. 2% Aqueous Sodium Peroxide.

Mgm. Taken	Mgm. Found	Mgm. per Liter	% Decomposition	Parts per million	Conc. Taken	Conc. Found	Time Shaken	Time of Standing
2.379	2.375	0.938	99.82	132	1/7575	1/7588	½ Hr.	Over night
1.983	1.979	0.768	99.79	108	1/9261	1/9280	½ Hr.	"
1.586	1.686	0.630	106.27	89	1/11236	1/10580	½ Hr.	"
1.189	1.283	0.407	107.89	58	1/17241	1/15053	½ Hr.	"
0.793	0.811	0.312	102.33	44	1/22727	1/22209	½ Hr.	"
0.713	0.758	0.281	107.71	40	1/25000	1/23210	¼ Hr.	"
0.594	0.459	0.230	95.76	32	1/31250	1/32633	¼ Hr.	2 Hr.
0.396	0.384	0.153	96.97	22	1/45454	1/46874	¼ Hr.	1 "
0.0396	0.416	0.157	104.91	22	1/45454	1/43327	¼ Hr.	1 "

An inspection of the table shows that in but one determination does the concentration taken and found differ by more than 3000. No. 4 gave a decomposition of 107.89% but the difference between the concentration of 1 part in 17,000. The lowest amount of dichlordiethyl sulphide taken was 0.396 mgm. and is equivalent to 0.5 c.c. N/100 silver nitrate. This then, is the limit of the method for the volumetric determination of the chloride unless larger bottles than the 2½-liter are used.

The advantages of the sodium peroxide method are:

(1) Decomposition takes place in the cold.

(2) No alcohol is necessary.

(3) Heating is unnecessary and the time needed to complete the analysis is shortened.

(4) Amounts of dichlordiethyl sulphide as low as 1 part in 45,000 may be analyzed.

SILVER NITRATE METHOD.

An aqueous solution of standard silver nitrate is an accurate means of determining dichlordiethyl sulphide. It has many advantages that commend its use as a quantitative method:

(1) Accurate results are obtained down to the practicable limits of volumetric analysis.

(2) The decomposition takes place in the cold.

(3) The method is rapid - a complete analysis can be made in about one hour.

(4) A standard solution is used as the absorbent, and

(5) An aqueous solution is used, thus avoiding the necessity of having to boil off any alcohol.

The Vacuum Bottle method was used in this work, and the following procedure was used.

An excess of approximately 100% of the silver nitrate necessary to completely precipitate all the chlorides

present is added to the bottle. The bottle may be shaken continuously for 30 minutes and immediately analyzed, or shaken for 5 minutes and allowed to stand over night. Satisfactory results are obtained by using either one of these methods. Shaking for 5 minutes and analyzing in 3 hours does not give comparable results. After decomposition, the contents of the bottle are transferred to an Erlenmeyer flask and the bottle is carefully washed with distilled water. Acidify with 7 - 10 cubic centimeters of concentrated nitric acid and coagulate the silver chloride, filter, wash, and cool. The excess silver nitrate is titrated with standard sodium thiocyanate, using 2 c.c. of ferric alum as the indicator.

The following results (Table 34) were obtained on a sample of dichlordiethyl sulphide which was 99.04% pure.

TABLE 34.

DETERMINATION DICHLORDIETHYL SULPHIDE WITH AQUEOUS SILVER NITRATE.

Gm. Dichlordiethyl Sulphide Taken	Gm. Dichlordiethyl Sulphide Found	% Decomposition	Mgm. of $Cl_2C_4H_8S$ per liter	P.P.M. by vol.	Conc. Taken	Conc. Found
0.0861	0.0847	98.4	34.40	4032	1/248	1/252
0.0414	0.04143	100.07	16.60	1945	1/514	1/510
0.0184	0.0183	99.8	7.3	855	1/1169	1/1171
0.0145	0.01452	100.06	5.9	679	1/1472	1/1471
0.0295	0.0293	99.3	11.8	1383	1/723	1/728
0.0283	0.0284	100.2	11.3	1324	1/755	1/753
0.0233	0.02334	100.2	9.3	1090	1/918	1/916
0.0477	0.04820	101.1	19.1	2238	1/438	1/433
0.0473	0.0478	101.1	18.9	2215	1/451	1/452
0.0321	0.0324	101.1	12.8	1500	1/666	1/658

[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Action of Aqueous Silver Nitrate on Low Concentrations of Dichlordiethyl Sulphide

Mgm. Dichlordiethyl Sulphide Taken	Mgm. Dichlordiethyl Sulphide Found	% Decomposition	Mgm. per liter $Cl_2C_4H_4S$ taken	P.P.M by Vol.	Conc. Taken	Conc. Found	Volume of Bottle c.c.
2.025	2.221	109.5	0.810	113	1/8848	1/8080	2583
1.690	1.862	110.2	0.67	93	1/1075	1/9770	2563
1.690	1.703	100.8	0.67	93	1/10752	1/10676	2583
1.352	1.475	109.1	0.54	75	1/1333	1/12220	2542
1.352	1.518	112.3	0.54	75	1/1333	1/11872	2563
1.352	1.341	99.2	0.54	75	1/1333	1/13441	2583
1.014	0.971	95.8	0.40	56	1/17368	1/18643	2550
1.014	1.072	105.8	0.40	56	1/17860	1/16881	2563
1.014	1.057	104.3	0.40	56	1/17860	1/17120	2550
0.840	0.842	100.3	0.33	46	1/21737	1/21672	2563
0.840	0.874	104.1	0.33	46	1/21737	1/20880	2583
0.840	0.915	108.8	0.33	46	1/21737	1/19988	2583
0.672	0.700	104.3	0.27	37	1/27027	1/26871	2542
0.504	0.573	113.8	0.20	28	1/35714	1/31383	2550
0.504	0.577	114.5	0.20	28	1/35714	1/31191	2542
0.504	0.513	101.9	0.20	28	1/35714	1/35048	2583
0.504	0.559	111.1	0.20	28	1/35714	1/32148	2542
0.336	0.250	74.4	0.134	18	1/55555	1/74671	2563
0.168	0.128	76.5	0.067	9	1/11111	1/14524	2550
0.168	0.200	119.3	0.067	9	1/11111	1/93136	2550

The silver nitrate method was extended to the analysis of lower concentrations of dichlordiethyl sulphide. Concentrations of 1 part in 25,000 can be accurately determined, and 1 part in 35,000 can be determined with a fair degree of accuracy. This is the limit of volumetric analysis when a sample is collected in a 2½-liter bottle. Samples of dichlordiethyl sulphide for these low concentrations were obtained by using aliquots from an alcoholic solution of the dichlordiethyl sulphide. The sample was dissolved in 25 c.c. of 95% alcohol and 25 c.c. of water and then diluted to volume in a volumetric flask. The size of volumetric flask used depends on the size of aliquots desired.

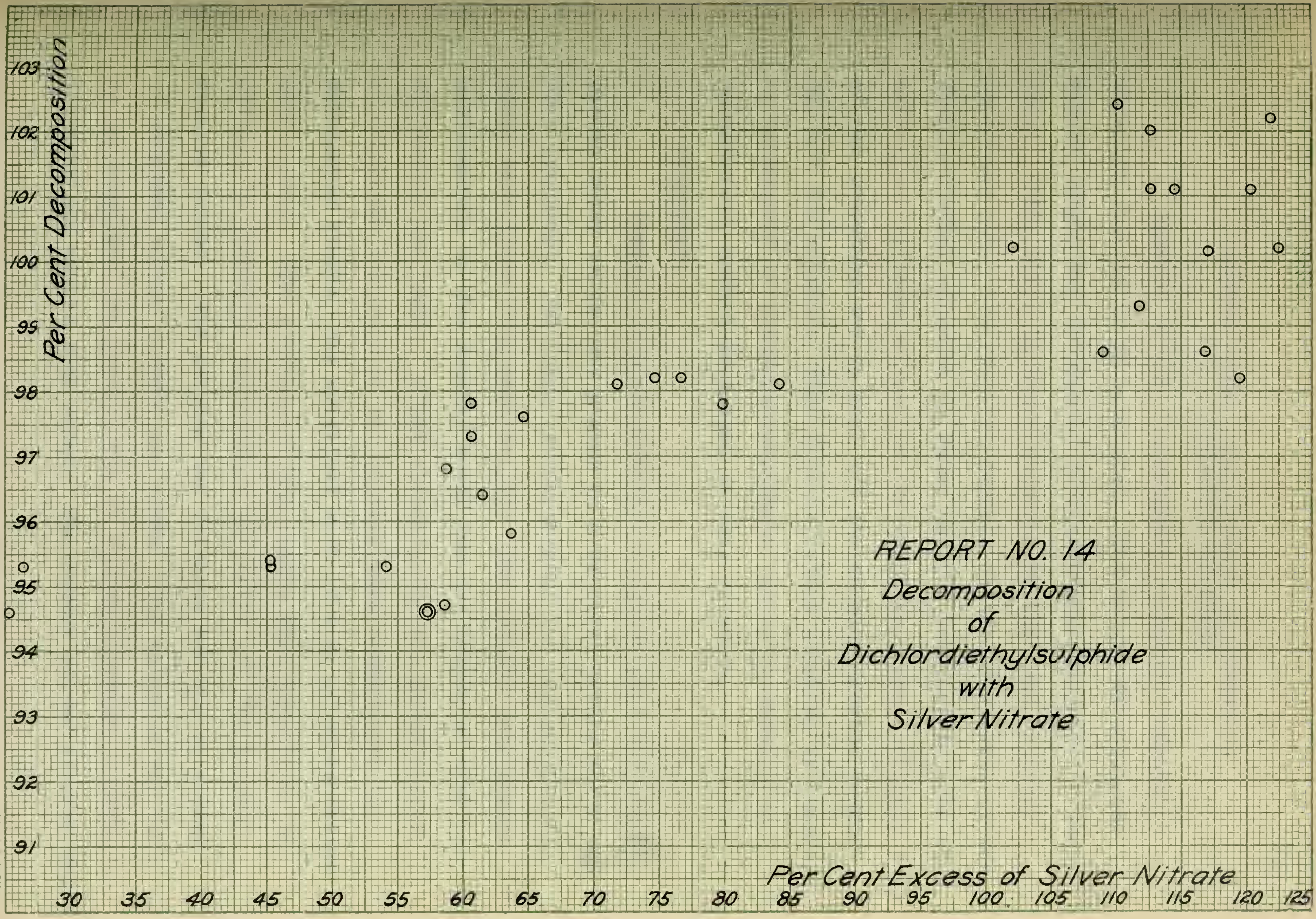
RELATION BETWEEN PERCENTAGE DECOMPOSITION AND EXCESS OF SILVER NITRATE USED TO DECOMPOSE DICHLORDIETHYL SULPHIDE.

The percentage decomposition and the per cent excess of standard silver nitrate added was noted in all the determinations made to determine a relation between the two if possible. From the results it was observed that uniformly poor results were obtained when the excess of silver nitrate used was below 57%. From 57% to 85% in excess gave on an average 94% to 98% decomposition, while 100% to 125% in excess gave 98% to 102% decomposition. It is therefore recommended that an excess of approximately 100% silver nitrate should be added to the amount necessary to decompose the dichlordiethyl sulphide.

TABLE 36.

RELATION OF EXCESS SILVER NITRATE TO PERCENT DECOMPOSITION OF DICHLORDIETHYL SULPHIDE

% Decomposition	% Excess of Reagent
95.3	21.5
94.6	25.3
95.3	45.3
95.4	45.3
95.3	54.1
94.6	57.3
94.6	57.3
94.7	58.6
96.8	58.7
97.3	60.6
97.8	60.6
95.8	63.6
97.6	64.6
98.1	71.8
96.4	61.5
98.2	76.7
98.2	74.7
97.8	79.9
98.1	84.1
100.2	102.1
98.6	109.0
102.4	110.1
99.3	111.8
102.0	112.7
101.1	112.7
101.1	114.5
98.6	116.9
100.16	117.1
98.2	119.5
101.1	120.3
102.2	121.9
100.2	122.5



REPORT NO. 14
Decomposition
of
Dichlordiethylsulphide
with
Silver Nitrate

U. OF I. S. S. FORM 3

AQUEOUS SODIUM THIOSULPHATE SOLUTIONS ON DICHLORDIETHYL SULPHIDE.

Aqueous sodium thiosulphate solutions varying in strength from 1% to 5% were used. The 3% and 5% solutions almost completely decomposed dichlordiethyl sulphide in the cold. After about 1½ hours standing in the cold, sulphur separates out. The reaction depends on the hydrolysis of the dichlordiethyl sulphide by water and the increase in rate of hydrolysis by means of sodium thiosulphate. The difficult part of the procedure was to boil off the sulphur dioxide andfilter off the sulphur. That dichlordiethyl sulphide is completely decomposed by sodium thiosulphate was later shown in a colorimetric method **developed** on this reaction.

Procedure:

Samples of Dichlordiethyl Sulphide were weighed in sealed glass bulbs, and placed in a 2½-liter bottle which was then evacuated. 50 cubic centimeters of the sodium thiosulphate were drawn into each bottle. The bottles were shaken continuously on the shaking wheel for the length of time indicated in the table. After standing for the given period of time, the contents of the bottles were transferred to Erlenmeyer flasks, and acidified with 10 c.c. of concentrated nitric acid. The contents of the flasks were boiled for 20 minutes to coagulate the sulphur and drive off the sulphur dioxide formed. The sulphur was filtered out and an excess of standard silver nitrate was added. The solution was heated to coagulate the precipitate of silver chloride, cooled, filtered and washed with water. The excess silver nitrate was

determined with standard sodium thiocyanate, using 2 - 3 c.c. ferric alum as the indicator.

TABLE 37.

ACTION OF SODIUM THIOSULPHATE ON DICHLORDIETHYL SULPHIDE.

Gm. $Cl_2C_4H_8S$ Taken	Time of Standing	Time Shaken	Strength of $Na_2S_2O_3$ Solution	Gm. $Cl_2C_4H_8S$ Found	% Decomposed or Hydrolyzed
0.0316	0 Min.	¾ Hr.	1%	0.0271	85.76
0.0420	20 "	¾ Hr.	1%	0.0383	91.20
0.0573	16 Hr.	½ Hr.	1%	0.0524	91.44
0.0621	16 "	½ Hr.	1%	0.0575	92.59
0.0300	16 "	1/3 Hr.	1%	0.0280	93.33
0.0622	36 "	½ Hr.	2%	0.0588	94.53
0.0592	36 "	½ "	2%	0.0566	93.91
0.0482	36 "	½ "	2%	0.0454	94.19
0.0378	12 "	½ "	3%	0.0363	96.03
0.0365	2 "	¾ "	3%	0.0349	95.61
0.0341	2 "	¾ "	3%	0.0326	95.60
0.0360	2 "	¾ "	3%	0.0~~3~~57 ?	98.84
0.0317	2 "	¾ "	3%	0.0322	101.57
0.0878	16 "	½ "	3%	0.0869	98.97
0.0446	12 "	1/3 "	5%	0.0421	94.40
0.0291	12 "	½ "	5%	0.0277	95.18
0.1066	16 "	½ "	5%	0.1033	96.90
0.0715	16 "	½ "	5%	0.0689	96.36

Although sodium thiosulphate is a neutral salt, the Mohr method could not be used because sodium thiosulphate is a solvent for silver chromate. Potassium chromate was added to a 3% sodium thiosulphate solution and no end point was obtained after 50 cubic centimeters of N/100 $AgNO_3$ had been added (Mellor, Quant. Anal. P. 80, 1913 Ed.)

TRICHLOROMETHYL CHLOROFORMATE.

Trichloromethyl chloroformate (superpalite), like chloropicrin, has a very high percentage of chlorine, and low concentrations of superpalite may be determined due to this fact. Superpalite is slowly hydrolyzed in the presence of water, the reaction is quite rapid at 100° C. Hydrolysis is greatly increased by alkalies and other neutral salts, among those giving the best results are sodium peroxide, sodium sulphite and silver nitrate. The action of these reagents in dilute solutions on low concentrations of Superpalite is given in detail.

Sodium Peroxide Method.

Samples of Superpalite were weighed in sealed glass bulbs and placed in 2½-liter bottles which were then evacuated. The bulbs were broken by shaking the bottle. 50 c.c. of ½%, 1%, 2%, and 4% aqueous solutions of sodium peroxide were used. The bottles were then shaken and allowed to stand a definite length of time. The standard sodium peroxide method of analysis was then carried out.

The results were quantitative with each concentration of sodium peroxide.

TABLE 38.

DETERMINATION OF TRICHLOROMETHYL CHLOROFORMATE WITH SODIUM PEROXIDE METHOD.

Gm. Super-palite Taken	Gm. Super-palite Found	Mgm. Super-palite per liter	Parts per Mil-lion. by vol.	Conc. Taken	Conc. Found	% De-Comp.
50 c.c. 4% Sodium Peroxide Shaken 30 Minutes. Time of Standing - Over Night						
0.0443	0.04496	17.44	1883	1/531	1/522	101.51
0.0562	0.05692	22.03	2495	1/400	1/394	101.32
0.0482	0.04849	19.4	2201	1/454	1/428	100.61
50 c.c. 4% Sodium Peroxide Shaken 30 Minutes. Time Standing - 1½ hour.						
0.0156	0.01579	6.16	698	1/1434	1/1417	101.21
0.0085	0.00850	3.36	381	1/2624	1/2624	100.000
0.0074	0.007524	2.92	341	1/2932	1/2871	101.68
0.0057	0.005751	2.25	255	1/3921	1/3921	100.08
50 c.c. 4% Sodium Peroxide Shaken 30 Minutes. Time Standing - ½ hour.						
0.0128	0.01288	5.06	573	1/1727	1/1716	100.6
0.0114	0.01137	4.5	510	1/1960	1/1966	99.73
50 c.c. 4% Sodium Peroxide Shaken 30 Minutes. (½ hour in bottle)						
0.0214	0.02173	8.42	955	1/1047	1/1036	101.08
0.0134	0.01321	5.29	600	1/1666	1/1700	98.06
50 c.c. 4% Sodium Peroxide Shaken 10 Minutes. (15 minutes in bottle)						
0.0155	0.01591	6.14	696	1/1436	1/1401	102.5
0.0274	0.02821	10.79	1223	1/817	1/791	103.2
50 c.c. 1% Sodium Peroxide Shaken 5 minutes and washed in bottle immediately.						
0.01775	0.01809	6.92	784	1/1275	1/1268	100.6
0.0126	0.01298	4.94	560	1/1785	1/1740	102.61

TABLE 38 (concluded).

50 c.c. ¼% Sodium Peroxide
Shaken 5 minutes and washed from bottle immediately.

Gm. Superpalite Taken	Gm. Superpalite Found	Mgm. Superpalite per liter	Parts per Million by vol.	Conc. Taken	Conc. Found	% Decomp.
0.0222	0.02211	8.77	996	1/1003	1/1008	99.59
0.0163	0.01670	6.41	727	1/1375	1/1343	102.45
0.0252	0.02503	10.0	1134	1/882	1/888	99.32

Trichloromethyl chloroformate in concentrations as low as 1 part in 800 is immediately decomposed by sodium peroxide as is shown in the above table (No. 38). The concentration of sodium peroxide required is very low, 0.125 gm. of sodium peroxide quantitatively decomposed 0.0252 gm. of trichloromethyl chloroformate.

Trichloromethyl chloroformate was collected in 2½-liter vacuum bottles from a gas chamber in which a known concentration of gas was present. The trichloromethyl chloroformate was drawn from the chamber into a burette over mercury, and transferred to the 2½-liter bottles. 50 cubic centimeters of 1% sodium peroxide were then drawn in and the bottle was shaken for 20 minutes and analyzed immediately. The results obtained are given in the following table (Table No. 39).

TABLE 39.

DETERMINATION LOW CONCENTRATIONS OF TRICHLOROMETHYL CHLORO- WITH SODIUM PEROXIDE

50 c.c. of 1% Sodium Peroxide
Shaken 20 minutes and analyzed immediately

Mgm. Superpalite Taken	Mgm. Superpalite Found	Mgm. per liter	Parts per million by vol.	Conc. Taken	Conc. Found	% Decomp.
2.468	2.431	0.~~0~~972	110	1/9090	1/9145	99.5
2.516	2.501	0.978	109	1/9092	1/9205	98.7
1.246	1.264	0.492	55	1/17676	1/17492	101.8
1.39	1.362	0.552	62	1/15873	1/16372	98.1
1.064	1.079	0.422	47	1/20408	1/20061	101.8
0.927	0.903	0.369	41	1/23831	1/24578	97.4
0.801	0.796	0.320	36	1/27289	1/27567	99.2
0.751	0.739	0.300	34	1/29428	1/30000	98.25
0.689	0.668	0.272	30	1/32258	1/32801	98.3
0.582	0.568	0.229	25	1/38819	1/39790	97.65
0.508	0.460	0.202	23	1/43500	1/48281	90.4

Gas concentrations of trichloromethyl chloroformate of 1 part in 25,000 may be determined accurately, whereas concentrations of 1 part in 30,000 can be determined with a fair degree of accuracy in samples collected in 2½-liter bottles.

SODIUM SULPHITE METHOD.

The standard sodium sulphite method was used for the analysis of trichlormethyl chloroformate. Weighed bulbs were placed in 2½-liter bottles which were then evacuated. The bulbs were broken by shaking the bottles. 50 c.c. of the alcoholic sodium sulphite were drawn in and the bottles were shaken continuously for ½ hour and allowed to stand over night. The results obtained showed that this method may be used with quantitative results (Table 40).

TABLE 40

DETERMINATION OF TRICHLOROMETHYL CHLOROFORMATE WITH SODIUM SULPHITE

50 c.c. Alcoholic Sodium Sulphite
Time shaken ½ hour Time Standing - Over night

Gm. Superpalite Taken	Gm. Superpalite Found	Mgm. Superpalite Found	Parts per Million by vol.	Conc. Taken	Conc. Found	% Decomposed
0.0494	0.04991	19.76	2235	1/447	1/446	100.09
0.0355	0.03144	12.6	1429	1/692	1/693	99.8
0.0232	0.02343	9.22	1046	1/956	1/954	100.18
0.0324	0.0328	12.7	1440	1/615	1/607	101.3

The time of standing with the sodium sulphite method was then shortened to two hours (table 41), after continuous shaking for 30 minutes. The trichloromethyl chloroformate in this case was also easily decomposed.

TABLE 41

50 c.c. Alcoholic Sodium Sulphite
Solution
Time Shaken ½ hour Time standing - 2 hours

Gm. Superpalite Taken	Gm. Superpalite Found	Mgm. per liter	Parts per Million by vol.	Conc. Taken	Conc. Found	% Decomposed
.0134	.01378	5.33	603	1/165	1/150	102.87
.0273	.02763	10.7	1213	1/824	1/815	101.09

Gas concentrations of trichloromethylchloroformate were drawn into a burette over mercury from a gas chamber

containing a known concentration of the gaseous trichloromethylchloroformate. The samples of gas were then transferred to 2½-liter vacuum bottles. 50 c.c. of alcoholic sodium sulphite were then drawn in, and the bottles were shaken continuously for 20 minutes and immediately analyzed according to the Standard Sodium Sulphite method.

The results were as satisfactory as with the sodium peroxide method (Table 42).

TABLE 42.

DETERMINATION LOW CONCENTRATIONS OF TRICHLOROMETHYLCHLOROFORMATE WITH SODIUM SULPHITE

50 c.c. of Alcoholic Sodium Sulphite
Shaken 20 minutes and immediately analyzed.

Mgm. Superpalite Taken	Mgm. Superpalite Found	Mgm. per liter	Parts per Million by vol.	Conc. Taken	Conc. Found	% Decomposition
2.809	2.702	1.11	126	1/7936	1/8250.6	96.11
2.536	2.489	1.002	113.5	1/8849	1/9030	98.
2.900	2.862	1.151	120.5	1/7615	1/7734	98.6
2.027	2.096	8.022	91.	1/10999	1/10770	102.1
2.189	2.102	8.65	98.2	1/10204	1/10605	96.2
1.014	1.007	0.404	45.7	1/21859	1/22063	99.3
1.026	1.017	0.403	45.7	1/22222	1/22441	99.15
1.010	1.005	0.402	45.6	1/21278	1/21182	99.5
0.949	0.936	0.478	42.7	1/23421	1/23781	98.7
0.728	0.708	0.287	32.5	1/31187	1/32053	97.25
0.564	0.546	0.221	25.	1/40018	1/41255	97.

The results showed that both the aqueous sodium peroxide and alcoholic sodium sulphite methods will give accurate results on gas concentrations as low as volumetric methods can be used. The sodium peroxide method is, however, much easier to use as

there is no alcohol or sulphur dioxide to boil off as in the sodium sulphite method. The sodium peroxide method is the easier and simpler method to use.

SILVER NITRATE METHOD.

Direct Method:

A sample of Superpalite was weighed out in a sealed glass bulb, and placed in a 1-liter glass stoppered bottle. 15 c.c. in excess of the standard silver nitrate necessary to precipitate the chlorine was added, the solution was acidified with 5 c.c. concentrated nitric acid. The bottle was shaken continuously for 20 minutes and after standing 20 minutes the contents were washed through a filter into an Erlenmeyer flask. 2 c.c. of ferric alum indicator were added and the excess silver nitrate was titrated with standard sodium thiocyanate.

1 c.c. N/10 $AgNO_3$- 0.004958 gm. of trichloromethylchloroformate.

TABLE 43.

DETERMINATION OF TRICHLOROMETHYLCHLOROFORMATE WITH SILVER NITRATE.

Gm. Super-palite Taken	Gm. Super-palite Found	Mgm. per liter	Parts per Million by vol.	Conc. Taken	Conc. Found	% Decom-position
0.0336	0.03336	33.6	3805	1/263	1/264	99.3
0.0391	0.0389	39.11	4428	1/226	1/227	99.5
0.02945	0.02975	29.45	3336	1/300	1/298	100.9
0.02595	0.02589	25.95	2939	1/340	1/341	99.8
0.02855	0.02873	28.55	3232	1/309	1/308	100.6
0.0043	0.004312	4.3	487	1/205	1/204	100.2
0.00905	0.00903	9.05	1025	1/976	1/977	99.9
0.0068	0.006791	6.8	770	1/1299	1/1301	99.8

VACUUM BOTTLE METHOD.

Weighed glass bulbs containing Superpalite were placed in 2½-liter bottles fitted with a rubberstopper, and standard silver nitrate was added to the bottle as in the Direct method. Consistently high results were obtained. When the rubber stoppers were examined the part exposed to the silver nitrate was considerably darkened. The high results obtained were due to the absorption of some silver nitrate by the rubber stoppers used. When the rubber stoppers used, were exposed for some time to the action of silver nitrate and then thoroughly washed with distilled water, good results were obtained.

Experiments were then conducted with 2½-liter Nela Vacuum Bulbs. The bulb of Superpalite was introduced and a glass tip sealed on. The bulb was then evacuated. On breaking the tip, the absorbing solution was drawn in and a rubber tubing connecting placed over the tip of the bottle. The results were very accurate.

TABLE 44.

SILVER NITRATE ON SUPERPALITE IN PRESENCE OF STOPPERS UNTREATED WITH SILVER NITRATE.

Gm. Superpalite Taken	Gm. Superpalite Found	Mgm. per liter	Parts per Million by vol.	Conc. Taken	Conc. Found	% Decomposition
0.0207	0.02205	8.28	904	1/11076	1/11794	106.56
0.0143	0.01623	5.72	647	1/15478	1/17512	113.49
0.0137	0.01497	5.48	620	1/16135	1/17624	109.27
0.0136	0.01533	5.44	616	1/16243	1/18436	113.45
0.0114	0.01269	4.56	516	1/19404	1/21605	111.31
0.0077	0.00912	3.08	348	1/38691	1/34163	118.7

TABLE 45.

SILVER NITRATE ON SUPERPALITE IN PRESENCE OF STOPPERS PREVIOUSLY TREATED WITH SILVER NITRATE.

Gm. Superpalite Taken	Gm. Superpalite Found	Mgm. per liter	Parts per Million by vol.	Conc. Taken	Conc. Found	% Decomposition
0.0189	0.0192	7.56	855	1/11693	1/11888	101.6
0.0771	0.0779	30.4	3440	1/291	1/291.2	100.1
0.0091	0.00907	3.64	412	1/2431	1/24206	99.6
0.0118	0.01199	4.72	534	1/1873	1/18932	101.

TABLE 46.

SILVER NITRATE ON SUPERPALITE IN VACUUM BOTTLE ALL OF GLASS.

Gm. Superpalite Taken	Gm. Superpalite Found	Mgm. per liter	Parts per Million by vol.	Conc. Taken	Conc. Found	% Decomp.
0.07115	0.07089	28.46	3214	1/309	1/310	99.6
0.0390	0.03821	15.6	1765	1/566	1/571	99.
0.0126	0.1259	5.04	570	1/1754	1/1763	99.8
0.0061	0.00613	2.44	276	1/3623	1/3605	100.5

The Nela Vacuum bulb is a satisfactory type of bottle to use for analyzing gas concentrations of trichloromethylchloroformate. If rubber stoppered bottles are used the stoppers should be previously treated (Compare Tables 44 and 45). The method of analysis is short and can be carried out in an hour. The L.P.G. Vacuum Bottle (Photograph No. 2) designed after this work was completed, may be used with better results than the Nela Bulbs.

CHLORACETOPHENONE.

Chloracetophenone is insoluble in water and is not hydrolyzed by it. Alkalies, however, such as sodium hydroxide will decompose it in the cold. Sodium peroxide decomposes chloracetophenone in the cold. Sodium sulphite does not completely decompose chloracetophenone, and sodium carbonate only partially decomposes chloracetophenone.

Sodium Peroxide Method.

Aqueous sodium peroxide will decompose chloracetophenone quantitatively, and it may therefore, be used as a method of analysis. The determinations were all conducted at the same time and treated under identical conditions. The stronger solutions of sodium peroxide were not as satisfactory as the weaker solutions.

Procedure:

50 cubic centimeters of aqueous sodium peroxide were poured into an Erlenmeyer flask, and the sample of chloracetophenone dissolved in alcohol was introduced. The flask was stoppered thoroughly, shaken and allowed to stand over night. The solution was warmed, and acidified with 5 cubic centimeters of concentrated nitric acid. An excess of standard silver nitrate was added to precipitate the chloride. The silver chloride was coagulated, filtered off and washed. 2 c.c. Ferric alum was added to the filtrate and the excess silver nitrate was titrated with standard sodium thiocyanate.

A blank determination was made along with the analysis.

TABLE 47.

ACTION OF SODIUM PEROXIDE ON CHLORACETOPHENONE.

50 c.c. 10% Aqueous Sodium Peroxide.

Mgm. Chloracetophenone	% CL_2 Found	% Decomposition
39.9	22.58	98.38
39.9	21.95	95.64
68.5	21.76	94.81
68.5	22.07	96.16
50 c.c. 5% Sodium Peroxide		
10.2	21.90	95.41
10.2	21.92	95.50
10.2	21.86	95.25
50 c.c. 2.5% Aqueous Sodium Peroxide		
10.2	22.42	97.69
10.2	22.49	98.01
10.2	22.49	98.01
10.2	22.60	98.48
50 c.c. 1% Aqueous Sodium Peroxide		
10.7	24.54	100.78
10.7	23.97	98.44
10.7	24.54	100.78
10.1	24.78	101.64
10.1	24.29	99.75

Action of Sodium Hydroxide on Chloracetophenone.

The standard aqueous sodium hydroxide method was used in the Direct method of decomposition on chloroacetophenone. Varying strengths of sodium hydroxide solutions were used. The chloracetophenone was dissolved in alcohol and aliquots were used for analysis. Sodium hydroxide

[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]		
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[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]		
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]		
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

[illegible]
[illegible]

[illegible]

solutions of 1%, 2%, and 5% strength were used. Blank determinations were made along with the analysis. The results obtained were accurate and quantitative (Table 48).

TABLE 48.

DETERMINATION OF CHLORACETOPHENONE WITH SODIUM HYDROXIDE.

CC. of Alcoholic solution of sample	Mgm. Sample	CC.N/100 $AgNO_3$	Percent Chlorine	Percent Decomposition
	50 c.c. 5% Aqueous Sodium Hydroxide			
10	10.172	6.71	23.39	101.96
10	"	6.56	22.86	99.65
10	"	6.71	23.39	101.96
10	"	6.71	23.39	101.96
10	"	6.56	22.86	99.65
	50 c.c. 2% Aqueous Sodium Hydroxide			
5	5.0365	2.48	24.41	100.24
5	5.0365	3.48	24.41	100.24
	50 c.c. 1% Aqueous Sodium Hydroxide			
10	10.073	6.96	24.49	100.57
5	5.0365	3.48	24.50	100.61
5	5.0365	3.48	24.50	100.61

ACTION OF ALCOHOLIC SODIUM SULPHITE ON CHLORACETOPHENONE

Decomposition was not complete with alcoholic sodium sulphite. The standard method was used in the Direct method in several experiments without success. The sodium sulphite and sample of chloracetophenone were allowed to stand over night before the analysis was made. The results obtained are as follows (Table 49):

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

TABLE 49.

ACTION OF SODIUM SULPHITE ON CHLORACETOPHENONE.

50 c.c. 3% Alcoholic Sodium Sulphite.

No.	CC. of alcoholic solution of sample	Mgm. of Sample	CC.N/100 $AgNO_3$ used	Percent Chlorine Found	Percent Decomp.
1	10	10.173	6.03	21.01	91.58
2	10	10.173	6.03	21.01	91.58
3	10	10.173	6.03	21.03	91.58
4	10	10.173	6.18	21.54	93.89
5	10	10.173	6.18	21.54	93.89

ACTION OF SODIUM CARBONATE SOLUTIONS ON CHLORACETOPHENONE.

1. Aqueous.

The action of aqueous sodium carbonate solutions of 1%, 2%, 3%, and 5% strength on chloracetophenone was quantitatively studied. Weighed amounts of chloracetophenone were placed into 2½-liter bottles. 50 c.c. of the aqueous sodium carbonate solution were added to each bottle and the bottles were shaken continuously on the shaking wheel for 30 minutes. The bottles were then allowed to stand for two hours. The solution was then filtered to remove any undecomposed chloracetophenone and the chloride was determined according to the standard sodium carbonate method.

TABLE 50

ACTION OF AQUEOUS SODIUM CARBONATE ON CHLORACETOPHENONE.

Na_2CO_3 sol.	c.c. used	Time Shaken	Time Standing	Mgm. Taken	Mgm. Found	% Decomposition
1%	50	30 min.	2 hr.	31.5	5.54	17.60
1%	50	30 "	2 "	33.3	8.32	25.00
1%	50	30 "	2 "	34.7	7.74	22.30
1%	50	30 "	2 "	36.8	9.45	25.70
1%	50	30 "	2 "	59.0	12.13	20.57
1%	50	30 "	2 "	81.9	18.00	21.99
2%	50	30 "	2 "	28.6	8.97	31.40
2%	50	30 "	2 "	32.5	10.80	33.20
2%	50	30 "	2 "	36.2	6.31	17.39
2%	50	30 "	2 "	44.7	11.40	25.50
2%	50	30 "	2 "	54.8	11.67	21.27
2%	50	30 "	2 "	55.9	9.27	16.60
3%	50	30 "	2 "	25.1	6.41	25.52
3%	50	30 "	2 "	25.8	5.05	19.60
3%	50	30 "	2 "	34.7	12.53	36.10
3%	50	30 "	2 "	44.6	8.60	19.30
3%	50	30 "	2 "	49.6	12.25	24.65
3%	50	30 "	2 "	50.0	12.70	25.40
5%	50	30 "	2 "	32.2	5.07	15.75
5%	50	30 "	2 "	33.7	6.50	19.30
5%	50	30 "	2 "	44.4	8.42	18.97
5%	50	30 "	2 "	46.0	12.08	26.25
5%	50	30 "	2 "	53.5	11.30	21.15
5%	50	30 "	2 "	58.0	12.85	22.15

Hot Aqueous Carbonate Solution.

Two samples of chloracetophenone were weighed into 200 c.c. glass stoppered bottles, and 50 c.c. of 1% aqueous solution of sodium carbonate were added. The bottles were immersed in hot water until the solid melted. Upon cooling, a turbid solution formed, which cleared upon acidifying. The usual determination for chlorine was made. The analysis showed that the chloracetophenone had been almost quantitatively decomposed.

TABLE 51.

ACTION OF HOT SODIUM CARBONATE SOLUTION ON CHLORACETOPHENONE.

Mgm. Chloracetophenone Taken	Found	% Decomposition
34.0	33.57	98.7
32.2	31.84	98.9

2. Alcoholic Sodium Carbonate.

The solutions used were 1%, 2%, 3%, and 5% sodium carbonate in 30% alcohol. The method of handling was the same as that used in the aqueous solutions except the alcohol was boiled off in each sample before acidifying with nitric acid. All of the solutions were turbid after filtering, but on warming to evaporate off the alcohol, the turbidity cleared up and the solutions turned a pale yellow color. This color

disappeared when the solutions were acidified with concentrated nitric acid in every case except in the sample weighing 319.2 mgm. This solution remained yellow and turbid, and therefore did not permit of an accurate determination.

The determinations were all made at the same time under identical conditions.

TABLE 52

ACTION OF ALCOHOLIC SODIUM CARBONATE ON CHLORACETOPHENONE.

Na_2CO_3 Sol.	C.C. Used.	Time Shaken	Time Stand	Mgm. Taken	Mgm. Found	% Decomp.
1%	50	30 min.	1½ hr.	29.0	24.50	84.40
1%	50	30 "	1½ "	34.8	27.54	79.20
1%	50	30 "	1½ "	35.0	31.60	90.20
2%	50	30 "	1½ "	34.7	25.50	73.50
2%	50	30 "	1½ "	123.3	41.50	33.65
2%	50	30 "	1½ "	319.2	88.50	27.80
3%	50	30 "	1½ "	27.6	18.07	65.40
3%	50	30 "	1½ "	36.0	24.80	68.90
3%	50	30 "	1½ "	50.7	37.80	74.60
5%	50	30 "	1½ "	36.2	30.60	84.50
5%	50	30 "	1½ "	44.1	27.17	61.60
5%	50	30 "	1½ "	48.2	38.65	80.25

The action of alcoholic and aqueous solutions of sodium carbonate is not quantitative but nevertheless very

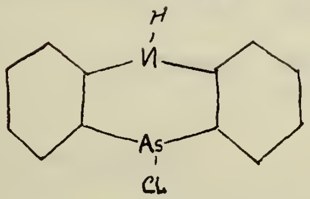
appreciable. For alcoholic solutions the decomposition varies from 60% to 85% for the various concentrations, while for aqueous solutions it varies from 15% to 33%, or approximately in the ratio of 3:1.

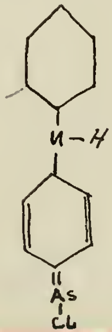
Action of Cold Water on Chloracetophenone.

To show that the action of aqueous and alcoholic solutions of sodium carbonate is not one of hydrolysis in the cold, some experiments were conducted. 50 c.c. of distilled water were added to samples that were weighed into 2½-liter bottles. These bottles were shaken continuously on the shaking wheel for ½ hour, 1 hour and 2 hours. The solution was filtered at once and titrated with standard silver nitrate for chlorides by the usual procedure. No decomposition had taken place. Similar samples were prepared and treated as before except that the filtrate was titrated with N/100 sodium hydroxide to test the formation of any hydrochloric acid. These results were also negative.

D. M.

D. M. has the empirical formula $C_{12}H_9N$ AsCl, the structure of this compound has not been definitely determined so that it has not been named. The structure may be one of the following:





The amount of chlorine present in D.M. is so low that a determination of the D. M. by this method is good only for higher concentrations. Using 0.3 c.c. of N/100 silver nitrate as the lowest titration that can accurately be made, it is possible to determine only 1 part in 15,000 by the halogen method. By the iodine titration method 1 part in 180,000 may be determined. For larger amounts of D. M. only, can a method for the chlorine determination be used.

Aqueous sodium peroxide, alcoholic sodium sulphite, aqueous sodium hydroxide and sodium ethylate solutions with D.M. always gave yellow solutions upon the addition of concentrated nitric acid. The end point was very poor and indistinct and it was necessary to use some other method of decomposition.

A satisfactory method was developed which destroyed the color and the D. M. itself by means of potassium permanganate. After this decomposition the chlorine was determined in the usual way. For higher concentrations the method is very accurate.

Solutions:

1. Glacial Acetic Acid.
2. N/10 $KMnO_4$ (approximately)
3. N/10 $H_2C_2O_4$ (")
4. N/100 Na CNS
5. N/100 $AgNO_3$
6. Conc. HNO_3 (1.42)

Procedure:

Weigh out a sample of D. M. into a bottle, and add

enough glacial acetic acid to dissolve it. Add an excess of N/10 $KMnO_4$ shake vigorously and allow to stand for 2-3 hours. Add 10 c.c. Conc. HNO_3 and an excess of N/100 $AgNO_3$. The nitric acid will prevent any silver oxalate from precipitating when the oxalic acid is later added. To hasten the reduction of the potassium permanganate and the manganese dioxide formed by the action of potassium permanganate on D. M., the solution should be hot when the oxalic acid is added. If the silver nitrate is not added before heating, some of the chloride may volatilize as hydrochloric acid. Heat the solution to boiling and add just enough N/10 $H_2C_2O_4$ necessary to clarify it. Expel all the acetic acid by boiling. If this is not done, a reddish yellow color will form when the ferric alum is later added. This boiling also coagulates the silver chloride precipitate. When the acetic acid is gone, add 2 c.c. of ferric alum as indicator and titrate the excess silver nitrate with 1/100 sodium thiocyanate.

A blank determination should be run using the same amount of solution as is used in the method. The purity of the sample used was 84.3%.

1 c.c. of N/100 $AgNO_3$ is equivalent to 2.7756 mgm. of D. M.

TABLE 53.

DETERMINATION OF D.M. BY PERMANGANATE METHOD.

Mgm. Sample	Mgm. D.M. Found	% D.M. Found	% Decomposition	Mgm. per liter	P.P.M.	Conc.
39.0	33.34	85.49	101.41	13.336	1076	1/929
16.0	13.54	84.60	100.36	5.416	437	1/2289
20.7	17.62	85.12	100.97	7.048	569	1/1760
49.4	41.82	84.66	100.43	16.728	1350	1/740
21.8	18.62	85.41	101.32	7.448	601	1/1663
34.5	29.50	85.51	101.43	11.800	952	1/1050
25.3	21.47	84.86	100.67	8.708	703	1/1422
23.5	19.96	84.94	100.76	7.864	635	1/1574
8.2	6.98	85.11	100.96	2.792	225	1/4444

Dichlordimethyl Ether.

Regnault[1] and Brochet[2] found that water, at least at ordinary temperatures, slowly decomposes dichlordimethyl ether giving hydrochloric acid as one of the products of hydrolysis. It was found that water appreciably hydrolyzes dichlordimethyl ether and that this hydrolysis was very nearly complete. Sodium peroxide decomposes the dichlordimethyl ether quantitatively.

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[1] Ann. 34, 31.
[2] Brochet. Ann. d. Chem. et phys. (7) 10 (1897)
[3] Zb. f. Chem. (1865) 1, 618.

Dichlordimethyl Ether.

Action of water.

The sample of dichlordimethyl ether was weighed in a glass bulb. This was placed in a 2-1/2 liter bottle and the later evacuated. The bulb was broken and 50 c.c. of water drawn in. The bottle was shaken on the shaking wheel for 1/2 hour and allowed to stand over night. The contents of the bottle were then washed into an Erlenmeyer flask and acidified with concentrated nitric acid. An excess of standard silver nitrate was added and the silver chloride formed was filtered off and washed. The excess silver nitrate was titrated with standard sodium thiocyanate using 2 c.c. of ferric alum as the indicator. A decomposition of 95.83% wasobtained.

Action of Aqueous Sodium Peroxide.

The procedure was the same as that given above, except 50 c. c. of 2% aqueous sodium peroxide were used instead of water.

TABLE 54.

DETERMINATION OF DICHLORDIMETHYLETHER WITH SODIUM PEROXIDE.

50 c.c. 2% aqueous sodium peroxide.

Sample No.	Dichlordimethyl Ether. Taken Gm.	Found Gm.	Percent Decomposition.
1.	0.0310	0.0309	99.67
2.	0.0588	0.0567	99.83
3.	0.0415	0.04144	99.85
4.	0.0446	0.04505	101.00
5.	0.0414	0.0415	100.2

BENZAL CHLORIDE.

For the analysis and decomposition of benzal chloride 3% solutions of aqueous sodium hydroxide, aqueous sodium peroxide, and alcoholic sodium sulphite were used. The sodium hydroxide and sodium sulphite method are equally good, but the sodium hydroxide method is much easier to carry out than the sodium sulphite method. The sodium peroxide method was unsatisfactory.

GENERAL PROCEDURE:

A sample of benzal chloride was weighed in sealed glass bulb. The bulb was placed in a 2½-liter bottle which was then evacuated, and the bulb broken. 50.c.c. of the absorbing solution was introduced. The bottles were shaken continuously on the shaking wheel for 20 minutes and allowed to stand for one hour. The contents of the bottle were transferred to an Erlenmeyer flask and the analysis was carried out according to the Standard Methods.

TABLE 55.

DETERMINATION OF BENZAL CHLORIDE WITH SODIUM HYDROXIDE.

50 c.c. 3% aqueous Sodium Hydroxide Used.

Gm. Benzal Cl. Taken	Gm. Banzal Cl. Found	% Decomposition	Mgm. per L. taken	Mgm. per L. Found	P.P.M. Taken	P.P.M. Found	Conc. Taken	Conc. Found
0.0900	0.0895	99.4	36.00	35.80	5011	4983	1/200	1/201
0.0181	0.1087	99.4	43.56	43.59	6063	6067	1/165	1/165
0.1387	0.0394	100.5	53.76	54.00	7483	7516	1/134	1/133
0.0958	0.0945	98.6	39.05	38.52	5435	5362	1/184	1/187
0.1203	0.1196	99.4	46.61	46.34	6488	6450	1/154	1/155
0.1353	0.1369	101.2	52.85	53.48	7356	7444	1/136	1/134

TABLE 56.

DETERMINATION OF BENZAL CHLORIDE WITH SODIUM SULPHITE.

50 c.c. 3% alcoholic sodium sulphite solution used.

Mgm. Benz. Cl. Taken	Mgm. Benz. Cl. Found	% Decomposition	Mgm. per liter	P.P.M.	Concentration taken	Concentration found
18.9	18.81	99.5	7.377	1027	1/974	1/979
11.8	11.72	99.3	4.609	642	1/1558	1/1569
16.4	16.22	98.9	6.394	890	1/1124	1/1136

TABLE 57.

ACTION OF SODIUM PEROXIDE ON BENZAL CHLORIDE.

50 c.c. 3% Aqueous Sodium Peroxide Vacuum Bottle Method.

Mgm. Benz. Cl. Taken	Mgm. Benz. Cl. Found	% Decomposition	Mgm. per liter	P.P.M.	Concentration Taken	Concentration Found
18.2	16.90	92.9	7.104	1608	1/622	1/669
16.8	16.22	96.5	6.562	1486	1/673	1/698
19.3	17.56	91.0	7.491	1696	1/590	1/648

50 c.c. 3% Aqueous Sodium Peroxide - Direct Method.

CC. N/10 $AgNO_3$ used.	Gm. Benzal Chloride Taken	% Decomposition
8.24	0.0724	91.60
8.19	0.0681	96.76
5.34	0.0454	94.62
5.95	0.0545	87.84
8.24	0.0752	88.19
5.54	0.0490	90.96

ANALYSIS OF MIXTURES OF GAS CONCENTRATIONS.

The advantage gained in using mixtures of various organic compounds in shell filling made it necessary to do considerable work in finding accurate methods for the determination of each compound in such mixtures. The method of collecting samples depended largely upon the method of analysis to be used. In some cases the properties of the components of the mixture were such that only single samples had to be taken. Aliquots of the absorbing solution after decomposition were used for determining the two components. More often it was necessary to collect duplicate samples, (Photograph No. 6) and each bottle was used to determine one of the constituents. It was necessary to carefully study the chemical reactions of each component of the mixture. The absorbing solution which was to be used to decompose one of the gases, had to be without action on the other gas present. It was necessary to determine the effect of various absorbing solutions by experiment.

The methods developed were the analysis of

1. Chloropicrin and Phosgene by the Sodium carbonate method
2. Phosgene and Cyanogen chloride
3. Chloropicrin and Dichlordiethylsulphide.

The method for determining Phosgene in the presence of Chloropicrin using Hexamine or Hexamethylene tetramine, in sodium hydroxide solution was studied and was shown to be inaccurate unless used as modified.

PHOSGENE AND CHLOROPICRIN: DETERMINATION OF PHOSGENE BY AN AQUEOUS SODIUM CARBONATE SOLUTION.

The determination of phosgene in the presence of chloropicrin must be accomplished by means of some absorbent which will quickly decompose the phosgene without having any effect on the chloropicrin. The experiments conducted with dilute aqueous solutions of sodium carbonate on chloropicrin showed that sodium carbonate could be employed in the presence of chloropicrin without any appreciable effect.

EXPERIMENTAL.

A sample of pure phosgene was obtained by vaporizing liquid phosgene over mercury, using an inverted funnel fitted with a stopcock at the end for this purpose. Samples for analysis were measured in a burette over mercury. The samples were drawn from the burette into evacuated 2½-liter bottles. 50 c.c. of 0.5% sodium carbonate solution were introduced and the bottles were shaken for 10 to 15 minutes. The contents of the bottles were immediately transferred to Erlenmeyer flasks and acidified with 5 c.c. concentrated nitric acid. An excess of standard silver nitrate solution was added and the solution warmed to coagulate the silver chloride. The precipitate was filtered off and washed. The solution was cooled, and the excess silver nitrate was titrated with standard sodium thiocyanate using 2 c.c. of ferric alum as the indicator.

TABLE 58.

DECOMPOSITION OF PHOSGENE WITH 0.5% SODIUM CARBONATE SOLUTION.

Phosgene Taken Gm.	Phosgene Found Gm.	Percent Decomposition
0.01100	0.01118	101.6
0.05168	0.05263	101.8
0.04257	0.04333	101.8
0.01736	0.01761	101.4
0.04629	0.04585	99.04
0.06986	0.07008	100.8
0.04671	0.04659	99.75
0.04366	0.03264	99.96

A number of determinations were made of phosgene in a mixture with chloropicrin. A weighed bulb of chloropicrin was introduced into the 2½-liter bottle before evacuation. After evacuation the bulb of chloropicrin was broken, causing it to vaporize. The phosgene was introduced from a gas burette as before. 50 c.c. of 1.5% aqueous solution of sodium carbonate were added. The bottles were shaken on the shaking wheel for 20 minutes and allowed to stand over night. The chloride content was then determined as above.

TABLE 59.

PHOSGENE IN PRESENCE OF CHLOROPICRIN.

50 c.c. 0.5% Aqueous sodium carbonate.

Phosgene corrected to 0° 760 mm.	Phosgene Taken	Chloropicrin Taken	Phosgene Found	Per cent Decomposition as $COCl_2$
8.14	0.0359	0.0338	0.0355	99.88
6.19	0.0273	0.1446	0.0268	98.17
7.05	0.0311	0.0474	0.0316	101.60
8.43	0.0372	0.0290	0.0368	98.92
7.00	0.0309	0.0360	0.0307	99.40
7.51	0.0331	0.0210	0.0335	101.20
8.83	0.0389	0.0345	0.0385	99.00
7.09	0.0313	0.0410	0.0317	101.25
6.95	0.0307	0.0373	0.0302	98.40
7.47	0.0330	------	0.0324	98.16
7.38	0.0326	------	0.0325	99.70
7.84	0.0346	------	0.0347	100.25
9.63	0.0425	------	0.0417	98.10
8.38	0.0370	0.0378	0.0366	98.92

The results show that with a dilute solution of sodium carbonate as the absorbing solution, phosgene can be quantitatively determined in the presence of chloropicrin. For the determination of concentrations in the field, duplicate samples were collected, the chloride due to phosgene was determined by the sodium carbonate method in one bottle, and the total chloride in the second bottle by the standard sodium peroxide or alcoholic sodium sulphite method.

PHOSGENE AND CHLOROPICRIN: Determination of Phosgene by Hexamine Solution.

A method of analysis of a mixture of phosgene and chloropicrin is given in Report M-31 Bureau of Mines. This

method states that:

> "A mixture of the two gases is drawn through three bottles, each containing 300 c.c. of a 2% alcoholic sodium sulphite solution; and the same amount of the gas through two bottles, each containing 300 c.c. of hexamine solution, (2% hexamine and 1% NaOH in aqueous solution). The former absorbs both phosgene and chloropicrin while the latter will only absorb phosgene."

The work conducted on the action of aqueous solutions of sodium hydroxide on chloropicrin, showed conclusively that even in dilute solutions it has a very appreciable effect on chloropicrin. Some work was carried out to see what effect the sodium hydroxide used in the hexamine solution has on the chloropicrin present. For low concentrations in the field this was very important.

EXPERIMENTAL.

The first experiment carried out was to see whether hexamine will decompose phosgene as effectively without the presence of sodium hydroxide as with it. A mixture of phosgene in air was used of approximately 1 : 1 composition; and also pure phosgene. The samples, were drawn into evacuated 2½-liter acid bottles. 50 c.c. of 2% hexamine solution were used on some samples, and 50 c.c. of 2% hexamine in 1% sodium hydroxide were used in the other samples. The bottles were shaken for 10 minutes and allowed to stand two hours. The results show that hexamine alone is as effective in decomposing phosgene as when it is used with sodium hydroxide.

After decomposition the contents of each bottle were transferred to an Erlenmeyer flask and acidified with 5 c.c. concentrated citric acid. An excess of standard silver

silver nitrate was added and the solution warmed to coagulate the silver chloride. The precipitate was filtered off and washed. The filtrate was cooled and the excess silver nitrate was titrated with standard sodium thiocyanate solution, using 2 c.c. of ferric alum as the indicator. A blank determination was made at the same time. In none of the blank determinations did the formaldehyde formed on boiling, affect the titration with silver nitrate or sodium thiocyanate.

TABLE 60.

HEXAMINE ON PHOSGENE WITH AND WITHOUT SODIUM HYDROXIDE.

C.C. of Air & Phosgene	Gm. of Gas as Phosgene	Gm. of Phosgene Found	Percent Phosgene	Sol. Used	Remarks.
5.6	0.0247	0.0120	48.40	2% Hex.	Mixture of air and Phosgene
3.76	0.0166	0.0082	49.15	"	"
5.67	0.0250	0.0121	48.38	"	"
4.49	0.0198	0.0097	48.90	"	"
4.12	0.0182	0.00855	47.55	2% Hex. & 1% NaOH	"
7.78	0.0343	0.0162	47.50	"	"
4.49	0.0198	0.00954	48.15	"	"
9.87	0.0436	0.0428	98.15	2% Hex.	Liquid Phosgene vaporized.
7.78	0.0344	0.0339	98.50	2% Hex. 1% NaOH	"

After determining that hexamine alone gave good results for the decomposition of phosgene, the method was tried on a mixture of phosgene and chloropicrin. The phosgene alone was determined. Chloropicrin was weighed out in

bulbs and placed into 2½-liter acid bottles which were then evacuated. Pure phosgene was drawn in. The bulb of chloropicrin was broken, and 50 c.c. of 2% hexamine solution was then added. The bottles were shaken for 10 minutes on the wheel and allowed to stand 15 hours. The chloride was determined as described above.

The presence of chloropicrin has no effect on the accuracy of the determination for phosgene. The concentration of chloropicrin in one case was eleven times that of phosgene, but the results were still very good.

TABLE 61.

HEXAMINE SOLUTION ON PHOSGENE IN THE PRESENCE OF CHLOROPICRIN

50 c.c. 2% Hexamine Solution

Gm. Chloropicrin Taken	Gm. Phosgene		Mgm. Phosgene per liter		Conc. Phosgene	
	Taken	Found	Taken	Found	Taken	Found
0.2910	0.0269	0.0233	10.44	10.99	1/422	1/402
0.0890	0.0219	0.0220	8.76	8.8	1/504	1/502
0.0450	0.0413	0.0416	16.29	16.4	1/271	1/269
0.0564	0.0096	0.0097	3.72	3.77	1/1187	1/1171
0.0750	0.0217	0.0218	8.56	8.6	1/516	1/513
0.1074	0.0227	0.0232	9.08	9.28	1/386	1/476
0.0580	0.0235	0.0236	9.07	9.11	1/487	1/485

The above work was repeated using 2% hexamine in a 1% sodium hydroxide solution. The presence of chloropicrin introduces a large error which depends upon the relative amounts of gases present and increases with the amount of chloropicrin. Hence this solution cannot be used to determine phosgene in the presence of chloropicrin, and this is

particularly true if the chloropicrin content is high.

TABLE 62.

HEXAMINE IN SODIUM HYDROXIDE ON PHOSGENE IN PRESENCE OF CHLOROPICRIN

50 c.c. 2% Hexamine in 1% Sodium Hydroxide Solution.

Gm. Chloropicrin Taken	Gm. Phosgene		Mgm. Phosgene per liter		Concentration $COCl_2$	
	Taken	Found	Taken	Found	Taken	Found
0.0514	0.0294	0.0361	11.41	14.00	1/387	1/314
0.0334	0.0235	0.0290	9.27	11.44	1/476	1/386
0.0284	0.0230	0.0278	9.02	10.9	1/489	1/405
0.0648	0.0220	0.0280	8.8	11.2	1/502	1/394
0.0422	0.0268	0.0303	10.57	11.95	1/418	1/369
0.0526	0.0238	0.0275	9.33	10.73	1/473	1/409
0.0460	0.0377	0.0430	14.8	16.86	1/298	1/262
0.1064	0.0096	0.0155	3.76	6.08	1/1175	1/726

To show the action of 2% hexamine and 2% hexamine in 1% sodium hydroxide solutions on chloropicrin, bulb samples of chloropicrin were placed in 2½-liter bottles. The bottles were evacuated and the bulbs broken. 50 c.c. of the 2% hexamine in 1% sodium hydroxide were used in some bottles, and the 2% hexamine solution in the remaining bottles. The bottles were shaken 30 minutes on the wheel and were allowed to stand 15 hours. The procedure for chlorides outlined above was then carried out.

Almost no decomposition took place in the presence of the 2% hexamine solution alone. When 1% sodium hydroxide was present, the amount of chloropicrin decomposed was sufficient to introduce a large error in the determination of phosgene in the presence of chloropicrin by the use of

hexamine in sodium hydroxide solution. It was found that a short period of shaking and standing resulted in considerable decomposition of chloropicrin. It is recommended for absorption methods, as well as other methods, that hexamine should not be used in sodium hydroxide solution for the analysis of this mixture.

TABLE 63.

ACTION OF HEXAMINE AND HEXAMINE IN SODIUM HYDROXIDE ON CHLOROPICRIN.

50 c.c. 2% Hexamine or
50 c.c. 2% Hexamine in 1% Sodium Hydroxide.

	Gm. Chloropicrin		% Chloropicrin	Mgm. Chloropicrin per liter		Concentration Chloropicrin.	
Solution	Taken	Found	Found	Taken	Found	Taken	Found
2% Hexamine & 1% NaOH	0.0224	0.00135	8.27	8.7	.71	1/845	1/10.356
"	0.0408	0.00335	8.22	16.1	1.32	1/456	1/5570
"	0.0662	0.00399	6.02	26.0	1.56	1/282	1/4712
"	0.0290	0.00174	6.02				
2% Hexamine	0.2780	0.00057	0.20	107.3	.22	1/685	1/33330
"	0.0330	0.00017	0.51	13.1	0.066	1/561	1/111100
"	0.0317	0.000115	0.36				
"	0.0856	0.000285	0.33				

STANDARD METHOD OF ANALYSIS OF FIELD SAMPLES OF MIXTURES OF PHOSGENE AND CHLOROPICRIN.

Field samples of mixtures of phosgene and chloropicrin are collected in duplicate by means of evacuated bottles. To one of the bottles add 50 c.c. of 1½% sodium peroxide solution, which will decompose both the phosgene and chloropicrin. To the second bottle add 50 c.c. of 2% aqueous solution of Hexamine which will decompose the phosgene. Both

samples should be shaken ½ hour on the wheel and allowed to stand for ½ to 1 hour before continuing with the analysis. Transfer the contents of the bottles to Erlenmeyer flasks. Acidify with 5 c.c. of concentrated nitric acid and add an excess of standard silver nitrate solution. Warm to coagulate the precipitated silver chloride, filter, wash, and cool. Titrate excess silver nitrate with standard sodium thiocyanate, using 2 c.c. of ferric alum as the indicator. Calculate the silver nitrate used by the sample decomposed by hexamine, to phosgene. Deduct chloride due to phosgene from total chlorides and calculate as chloropicrin.

PHOSGENE AND CYANOGEN CHLORIDE.

The determination of a mixture of phosgene and cyanogen chloride is a difficult problem in both high and low concentrations. The determination of low gas concentrations in the field is difficult because the physical and chemical properties of both substances are somewhat similar. The reagents which will react with one gas, will in the majority of cases react with the other.

Phosgene reacts with aniline to form diphenyl urea, a compound which is stable in the presence of dilute alkalies, such as barium hydroxide. Cyanogen chloride reacts with aniline to form an addition product known as the hydrochlorate of melaniline.[#] It was thought that dilute alkali would decompose melaniline and experiments were first conducted to

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[#] Jour. Chem. Soc. 1, 285 and 7, 184.

determine this.

Duplicate samples of cyanogen chloride were measured from a gas burette into evacuated 2½-liter bottles. 25 c.c. of a 5% solution of pure aniline in dry benzene were added to one bottle and it was vigorously shaken and allowed to stand until the production of melaniline was complete. Both bottles were then treated with an excess of N/50 barium hydroxide solution, shaken, and allowed to stand till complete decomposition had been effected. The excess alkali was titrated with N/50 nitric acid and the amount of barium hydroxide used up in each case was calculated and found to be the same. N/50 barium hydroxide therefore, decomposes melaniline quantitatively. This difference in the properties of phosgene and cyanogen chloride is made the basis of the method employed for analyzing a mixture of the two.

If duplicate samples of a mixture of phosgene and cyanogen chloride are taken, and to one bottle a solution of aniline in benzene is added, and both bottles are then treated with an excess N/50 barium hydroxide, the difference in the amount of barium hydroxide used up will represent that part of the phosgene which is held in combination as dephenyl urea. This difference in titration is equivalent to one CO_2 group from phosgene, and consequently one molecule of barium hydroxide is equivalent to one molecule of phosgene.

(1) $COcl_2 + 2C_6H_5NH_2 = CO(NHC_6H_2) + 2HCl$

(2) $2HCl + Ba(OH)_2 = BaCl_2 + 2H_2O$

(3) $COCl_2 + 2Ba(OH)_2 = BaCO_3 + BaCl_2 + 2H_2O$

(4) $COCl_2 + H_2O = CO_2 + 2\ HCl$

(5) $CO_2 + 2HCl + 2Ba(OH)_2 = BaCO_3 + BaCl_2 + 3H_2O$

(6) $CNCl + 2C_6H_5NH_2 = C_{12}H_{13}(CN)\ N_2HCl$

(7) $2CN\ Cl + 2Ba(OH)_2 = BaCl_2 + Ba(CNO_2) + 2H_2O$

To arrive at this result, subtract equation number (2) from equation number (5).

Equation No. 3 indicates the formation of barium carbonate when phosgene is treated with barium hydroxide. As the excess of barium hydroxide must be titrated with standard nitric acid it would be necessary to either filter off the barium carbonate precipitate or else make up to volume and allow it to settle, if it interfered in the titration.

The effect of barium carbonate on the titration of N/50 barium hydroxide with N/50 nitric acid, using phenolphthalein as the indicator, was determined by preparing some chemically pure barium carbonate. Some of the pure barium carbonate was added to 25 c.c. of $^N/50$ barium hydroxide in an Erlenmeyer flask. 25 c.c. of the $^N/50$ barium hydroxide alone was added to a second flask. The titration was carried out to a colorless end point in both cases. As was expected the results were the same, the color change with phenolphthalein being on the alkaline side, there was no free acid present to react with the carbonate until the excess alkali had been used up and the end point was passed. The fact that the excess barium hydroxide can be satisfactorily titrated in the presence of barium carbonate made it possible to perform the titration with the nitric acid in the same bottles in which the gas samples were collected and decomposed.

A known mixture of phosgene and cyanogen chloride was prepared by filling thick walled glass bulbs with the liquified compounds. The bulbs were weighed before and after filling. The bulbs were introduced into a 20-liter bottle, the bottle was partially evacuated. The bulbs were broken and the bottle was allowed to stand for 16 hours. The stopcock of the bottle was then opened and filled with air, and allowed to stand six hours before using; (the room was kept at constant temperature). The cyanogen chloride contained 5% hydrocyanic acid which did not interfere with the determination in any way.

The following method was used: A duplicate sample was introduced into evacuated 2½-liter bottles. To one bottle 25c.c. of 5% aniline in dry benzene was added, and the bottle shaken for 15 minutes, and allowed to stand for ½ hour. An excess of $^N/_{50}$ barium hydroxide was then added to each bottle, using phenolphthalein as the indicator. The bottles were shaken 15 minutes and allowed to stand over night. The excess alkali was then titrated with $^N/_{50}$ barium hydroxide used in the two bottles was calculated as phosgene. The contents of the bottle to which only barium hydroxide had been added was then used to determine the total chlorides. The solution was acidified with nitric acid, and boiled to destroy the cyanic acid. An excess of standard silver nitrate was then added and the silver chloride was coagulated, filtered off and washed. The excess silver nitrate was titrated with standard sodium thiocyanate using 5 c.c. of ferric alum as the indicator. The amount of chloride due

to phosgene was subtracted from the total chloride, and the difference was calculated to cyanogen chloride.

TABLE 64.

No.	Mgm. cyanogen Chloride Taken	Mgm. Phosgene Taken	Mgm. Cyanogen Chloride Found	Mgm. Phosgene Found	% Recovered. Cyan.	Phos.
1	14.97	14.79	14.14	15.65	94.5	103.0
2	13.98	13.73	13.77	13.96	98.4	101.6
	Mgm. per Liter		Parts per Million		Conc.	
1	5.98	5.87	2180	1330	1-458	1-753
2	5.58	5.51	2035	1248	1-490	1-800

The results for concentrations containing 1 part of cyanogen chloride in 500, and phosgene 1 part in 800 are very satisfactory. As the limits of the method depend upon the determination of the phosgene, lower concentrations of phosgene in the mixture were used. At a concentration of 1 part in 1500 of phosgene the determination of phosgene ceases to be accurate and the percent of phosgene found drops considerably.

TABLE 65.

	Mgm. Cyanogen chlor- Taken	Mgm. Phosgene Taken	Mgm. Cyanogen Chloride Found	Mgm. Phosgene Found	% Recovered	
					Cyan.	Phos.
No.						
1	18.55	7.47	16.23	8.02	87.5	107.2
2	13.40	5.40	14.38	4.17	107.0	77.2
3	12.10	3.88	14.63	1.75	121.2	35.8
	Mgm. per Liter		Parts per Million		Concentration	
1	7.42	2.98	2700	675	1/370	1/1480
2	5.36	2.16	1950	488	1/512	1/2050
3	4.83	1.96	1760	443	1/568	1/2250

CHLOROPICRIN AND DICHLORDIETHYL SULPHIDE.

The basis for a method of determining chloropicrin and dichlordiethyl sulphide depends on the fact that sodium peroxide quantitatively decomposes both, while silver nitrate will decompose only the dichlordiethyl sulphide. The total chlorides are determined in one sample, and the chloride due to dichlordiethyl sulphide is so low that the highest possible concentration at 25° C. is only about 1 part in 14,000. Its persistency, however, is much greater than that of chloropicrin. Evacuated 2½-liter bottles were used. The L.P.G. Vacuum bottle which has no rubber stopper was used for the silver nitrate determination of the dichlordiethyl sulphide to avoid the loss of any silver nitrate. The use of 500 c.c. glass

stoppered bottles would be very satisfactory for the direct analysis of the mixture.

EXPERIMENTAL.

(A) Sodium Peroxide Method.

Glass bulbs of chloropicrin and dichlordiethyl sulphide were placed in a 2½-liter acid bottle. The bottle was then evacuated, and the bulbs broken by shaking. 50 c.c. of 2% aqueous sodium peroxide solution were then drawn in. The bottles were shaken on the wheel for ½ hour and allowed to stand over night. The contents of the bottle were transferred to an Erlenmeyer flask and acidified with 7 c.c. of concentrated nitric acid. An excess of standard silver nitrate was then added and the precipitated silver chloride was coagulated, filtered and washed. The filtrate was cooled, and the excess silver nitrate was titrated with standard sodium thiocyanate using 2 c.c. of ferric alum as the indicator.

TABLE 66.

DETERMINATION OF TOTAL CHLORIDE IN CHLOROPICRIN AND DICHLORDIETHYL SULPHIDE MIXTURE WITH 2% SODIUM PEROXIDE.

Gms.	Gms.	% Mixture		% Total	Ratio	
CCl_3NO_2 Taken	$Cl_2C_4H_8S$ Taken	CCl_3NO_2	$Cl_2C_4H_8S$	Cl. Found	CCL_3NO_2	$Cl_2C_4H_8S$
0.0251	0.0238	51.33	48.67	99.76	1	- 1
0.0274	0.0263	51.02	48.98	99.82	1	- 1
0.0207	0.0227	47.70	52.30	99.36	1	- 1¼
0.017	0.0251	40.38	59.62	98.96	1	-1¼
0.0142	0.0170	45.51	54.49	98.82	1	- 1
0.0577	0.0473	54.95	45.05	99.21	1¼	- 1
0.0217	0.0174	55.49	44.51	99.05	1¼	- 1
0.0205	0.0215	51.19	48.81	99.20	1	- 1
0.0351	0.0392	47.24	52.76	98.96	1	- 1
0.0115	0.0120	48.93	51.07	99.17	1	- 1

(b.) $^N/10$ SILVER NITRATE METHOD IN L.P.G. VACUUM BOTTLE.

The tip of the L.P.G. Vacuum bottle was cut off so that weighed bulbs of chloropicrin and dichlordiethyl sulphide could be inserted. The tips were then sealed on and a piece of rubber tubing fitted with a clamp inserted on the top. The bottle was evacuated and the bulbs broken by shaking. An excess of approximately 100% of standard silver nitrate was then drawn into the bottle. The bottle was shaken for 15 - 20 minutes and allowed to stand over night. The contents of the bottle were transferred to an Erlenmeyer flask and 7 c.c. of concentrated nitric acid were added. The precipitate of silver chloride was coagulated, filtered, and washed. The filtrate was cooled, and the excess silver nitrate was titrated with standard sodium thiocyanate solution using 2 c.c. of ferric alum as the indicator.

The following results were obtained for dichlordiethyl sulphide:

TABLE 67.

DETERMINATION OF DICHLORDIETHYL SULPHIDE CHLOROPICRIN MIXTURE.

Time Standing - 12 hours.

Gms. CCl_3NO_2	Gms. $Cl_2C_4H_8S$	% Mixture CCl_3NO_2	% Mixture $Cl_2C_4H_8S$	% $Cl_2C_4H_8S$ Found	Conc. $Cl_2C_4H_9S$ T'kn.	Conc. $Cl_2C_4H_9S$ F'nd	Ratio CCl_3NO_2:Cl_2C_4
0.0380	0.0156	70.90	29.10	100.10	1/1150	1/1150	1 - 3
0.0323	0.0338	48.86	51.14	98.29	1/526	1/550	1 - 1
0.0505	0.0518	76.17	23.83	100.25	1/1120	1/1120	3 - 1
0.0200	0.0239	45.56	54.44	99.08	1/733	1/757	1 -1-1/5

A differential method of analysis of a mixture of chloropicrin and dichlordiethyl sulphide has been used with quantitative results. Varying the percent of either component of the mixture does not affect the results at all. Decomposition takes place in the cold and the analysis may be very easily carried out.

SUMMARY.

The problem of determining low concentrations of organic compounds under field conditions was solved by carefully studying the reactions of each compound and developing methods of analysis from the results obtained.

The sodium peroxide and sodium amalgam methods for determining chloropicrin were developed and compared with the sodium sulphite method. These methods were used for determining low concentrations of chloropicrin. The use of dilute solutions of sodium peroxide in organic analysis was introduced in the analysis of chloropicrin concentrations. The sodium peroxide gave excellent results in the hands of different observers. Dilute solutions of sodium peroxide were used with good results. The action of aqueous and alcoholic solutions of sodium hydroxide and sodium carbonate on chloropicrin was carefully studied. Alcoholic sodium hydroxide will decompose about 66% of the chloropicrin, whereas the alcoholic sodium carbonate decomposes about 35% of the chloropicrin.

Brombenzyl cyanide was determined in low concentra-

tions, by the alcoholic sodium hydroxide, aqueous sodium peroxide, and sodium ethylate methods. The action of sodium sulphite was not quantitative.

Dichlordiethyl sulphide was determined by the aqueous sodium peroxide and standard silver nitrate methods. Quantitative results were not obtained in the cold by using sodium hydroxide or sodium sulphite. Sodium thiosulphate will decompose dichlordiethyl sulphide quantitatively.

The sodium peroxide, sodium hydroxide, silver nitrate, and sodium sulphite methods gave accurate results in the analysis of trichlormethyl chloroformate concentrations. The ease with which the sodium peroxide method could be carried out, made it the desirable method to use.

Chloracetophenone was accurately determined by using the sodium peroxide and sodium hydroxide methods of analysis. The sodium sulphite method was unsatisfactory. The action of aqueous and alcoholic solutions of sodium carbonate in the cold on chloracetophenone was carefully studied. Aqueous solutions when heated will decompose chloracetophenone.

D. M. cannot be determined by the action of sodium peroxide, sodium hydroxide, or sodium sulphite, with the subsequent determination of the chloride by the Vohlhard method, due to the formation of a colored compound. A method for the determination of D. M. was developed by decomposing it with potassium permanganate.

Dichlordimethyl ether was readily determined by means of the aqueous sodium peroxide method.

Benzal chloride was determined with the sodium hydroxide and sodium sulphite methods. The sodium peroxide method did not give quantitative results.

Mixtures of phosgene and chloropicrin were analyzed by methods that were thoroughly studied to note any limitations. It was shown that the hexamine in sodium hydroxide not only decomposes the phosgene but appreciably attacks the chloropicrin. This method was accordingly modified. A method for analyzing a cyanogen chloride and phosgene mixture was developed which gives accurate results for the higher gas concentrations. Methods of analysis of chloropicrin and dichlordiethylsulphide; chloropicrin and trichlormethylchloroformate mixtures were worked out and shown to be accurate.

II. SODIUM PEROXIDE AS A REAGENT IN MICROCHEMICAL ANALYSIS.

The oxidation of chloropicrin by aqueous solutions of sodium peroxide gives sodium chloride and sodium nitrate as part of the products of oxidation. The determination of the sodium nitrate formed is the basis of a colorimetric method for the determination of chloropicrin. The colorimetric methodis as accurate as the volumetric methods used for the determination of chloropicrin, and may be applied in low concentrations where volumetric methods cannot be used.

It was necessary to modify the outlined phenoldisulphonic acid methods for the determinations of nitrates, to make this method applicable for the analysis of low concentrations of chloropicrin. In the first experiments that were carried out, strong solutions of sodium peroxide were used to decompose the chloropicrin. The weighed bulbs of chloropicrin were placed into 2½-liter bottles which were then evacuated. The sodium peroxide solution was drawn in as in the Vacuum Bottle method, and the bottles were thoroughly shaken. The decomposition mixture was transferred to volumetric flasks and made up to volume, and aliquots containing 0.01 - 0.02 mgm. of nitrogen were pipetted off and evaporated to dryness on the water bath. The residue was incorporated with 2 cubic centimeters of phenol di-sulphonic acid and washed into a Nessler tube. The solution was made strongly alkaline with ammonium hydroxide and made up to a volume of 50 cubic centimeters. A standard was prepared in

the same manner, using a standard solution of sodium nitrate containing 0.01 mgm. of nitrogen per cubic centimeter.

No color was obtained using the above procedure. It was found that the residue obtained on evaporating the aliquot of the decomposition solution was so strongly alkaline that it completely neutralized the 2 c.c. of phenol di-sulphonic acid, and therefore nitration could not take place. To overcome this difficulty, the aliquot solutions were almost neutralized with sulphuric acid (1:1) before evaporation. The results obtained in using this procedure were not quantitative.

The interference of chlorides in this method is well established in the literature. It is stated, however, in some of the standard methods that removal of chlorides may be omitted if the sample contains less than 30 parts per million. Chlorides are present, due to the decomposition of the chloropicrin and from the chemicals used in the determination. The presence of 30 parts per million of chlorine is equivalent to 50 milligrams of chloropicrin; Quantitative results could not be obtained without removing all the chloride, even when present in very small amounts. The addition of ammoniacal silver sulphate to combine with the chlorides present improved the results somewhat but did not make them quantitative.

An aqueous solution of silver sulphate was added to the decomposition mixture after making it slightly acid with 1:1 sulphuric acid. The silver chloride was filtered off and the filtrate was made slightly alkaline with 25%

sodium hydroxide solution. The silver oxide formed was filtered off, and the filtrate made up to definite volume. Aliquot portions were evaporated to dryness and the residue incorporated with 2 c.c. of phenol di-sulphonic acid and washed into a Nessler tube. After making the solution alkaline with amonium hydroxide and diluting it to a volume of 50 c.c., it was compared with a standard prepared from sodium nitrate. The results obtained were quantitative.

When the concentrations of chloropicrin to be determined were very low, it was necessary to evaporate large aliquots to obtain a reading. The residue was too large to incorporate with 2 c.c. of phenol di-sulphonic acid due to the strong solutions of sodium peroxide used. Further experiments showed that low concentrations of sodium peroxide (¼%) might be used to decompose chloropicrin. When the lower concentrations of chloropicrin were used, there was no further trouble with a residue, that could not be easily incorporated with 2 c.c. of phenol di-sulphonic acid.

Modified Phenol Di-sulphonic Acid Method.

Solutions required.

1. Phenol di-sulphonic acid.[1]

Dissolve 25 grams of pure white phenol in 150 c.c. of pure concentrated sulphuric acid, add 75 c.c. of fuming sulphuric acid (15 per cent SO_3), stir well, and heat for two hours at about 100 C.

2. Standard silver sulphate solution.

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[1] D.S. Pratt. Jour. Am. Chem. Soc. Aug. 1909, Mar. 1910, Mar. 1911.

Dissolve 4.4 grams of silver sulphate, free from nitrate, in 1 liter of water. One c.c. of this solution is equal to 1 mgm. of chloride.

3. Sulphiric Acid 1:1
4. Sodium Hydroxide 25%
5. Ammonium Hydroxide (sp. gr. 0.9)
6. Standard Nitrate Solution.

Dissolve 0.7217 gram of KNO_3 or 0.6068 gram of $NaNO_3$ in one liter of distilled water; after making up to volume and thoroughly shaking, 10 c.c. are pipetted off, placed in a 100 c.c. volumetric flask and diluted to volume.

One c.c. of this solution is then equivalent to 0.01 milligram of nitrogen. If desired 0.6151 gram of KNO_3 or 0.5171 gram of $Na\,NO_3$ may be dissolved in one liter of distilled water. 10 c.c. are then pipetted off, added to a 100 c.c. volumetric flask, and made up to volume. One c.c. of this solution is equivalent to 0.1 milligram of chloropicrin directly.

Procedure.

The contents of the bottle in which the decomposition has been carried out are transferred to a beaker and the bottle is carefully washed. The contents of the beaker are made very slightly acid with the 1:1 sulphuric acid, using litmus paper as the indicator. The sulphuric acid should be added from a burette, as a few drops in excess will require the addition of more sodium hydroxide for neutralization. This not only increases the volume of solution to be

evaporated, but increases the amount of residue that must be incorporated with the 2 c.c. of phenol di-sulphonic acid.

The beaker is placed on a steam bath and brought almost to boiling. The solution should not be allowed to boil as it might result in the loss of nitration as nitric acid. Enough silver sulphate solution is added to precipitate all the chlorides and about 5 c.c. in excess. The silver chloride is coagulated and removed by filtration. Chloride free paper should be used, and it is always desirable to first wash the paper with distilled water before using it for filtration. Wash the precipitate.

The filtrate and washings are cooled and made very slightly alkaline with the sodium hydroxide solution, added from a burette, using litmus paper as the indicator. The solution is boiled to coagulate the precipitate and decrease the volume. After cooling, the precipitate of silver oxide is filtered off and the filtrate is caught in a volumetric flask of proper capacity. The solution must be cooled before filtering because the solubility of silver oxide is greater in hot solutions than in cold. Accordingly, contamination of silver oxide is met with when the solution is filtered in the cold. Often the silver oxide passes thru the paper in a semi-colloidal condition, but this was prevented by keeping the funnel well filled during filtration and by using a small amount of sodium hydroxide in the wash water.

The solution in the volumetric flask is diluted to volume and thoroughly shaken. An aliquot or entire contents

(depending on the amount of chloropicrin decomposed) of the flask are pipetted off and added to a porcelain evaporating dish. The liquid is evaporated to dryness on the steam bath. After cooling, exactly 2 c.c. of the phenol di-sulphonic acid are added to the residue from a calibrated pipette. The residue and reagent are thoroughly incorporated, using a glass rod. If the residue is compact, the solution of the residue may be aided by placing the dish on the steam bath and rubbing constantly with a glass rod. In no case should the dish be left on the water bath longer than two minutes. It was observed that longer warming introduced considerable errors.

Cool the residue if it has been warmed, and wash the contents of the dish into a Nessler tube. The solution is diluted to 40 c.c. with distilled water and made up to the 50 c.c. mark with concentrated ammonium hydroxide. The cylinder is shaken and the contents of the tube are filtered and compared in a colorimeter with a standard color.

BLANK.

A blank determination must be made on the materials used in the determination itself. The nitrogen content of the reagents is especially important when the concentration of chloropicrin is very low. Nitrate-free reagents should be used as much as possible. The same quantity of sodium peroxide solution as is used in the determination is measured into an Erlenmeyer flask. The same amount of sulphuric acid and silver sulphate are added. The silver chloride is filtered off, the same amount of sodium hydroxide

is added, and the silver oxide formed is filtered off. The filtrate is caught in an evaporating dish, and the total filtrate evaporated to dryness and the residue treated as in the procedure. The smaller the amount of chloropicrin, the greater effect the blank will have on the determination. It is suggested that for low concentrations of chloropicrin, the same aliquot of a blank solution be evaporated to dryness as is evaporated in the determination itself.

PREPARATION OF STANDARD COLORS.

The standard colors are prepared from the standard nitrate solution. If a standard which should represent 0.02 milligrams of nitrogen is desired, 2 c.c. of the standard nitrate solution (1 c.c. = .01 mgm. of nitrogen) are pipetted off, placed in a clean evaporating dish and evaporated to dryness. After cooling, exactly 2 c.c. of phenol di-sulphonic acid are added from a pipette, and the residue is very thoroughly incorporated with the acid, without warming if possible, but in no case should the warming be continued over two minutes. After cooling, the reaction mixture is washed into a 50 c.c. Nessler or specimen tube, made up to 40 c.c. with distilled water, and filled to the mark with the ammonium hydroxide solution. The tube is then well shaken, filtered, and compared in a colorimeter with the unknown solution similarly treated. Standards prepared in this way are not permanent standards, but should be made up fresh for each series of determinations.

Experimental.

A saturated solution of sodium peroxide was first used for the decomposition of chloropicrin for the nitrate determination. Weighed bulbs of chloropicrin were placed into 2½-liter bottles which were then evacuated, and 50 c.c. of the sodium peroxide solution were drawn in. The bottles were shaken and allowed to stand for the indicated length of time. The results obtained are given in the following table.

Under the colum "remarks", it is noted that in some cases no colorimeter was used. The colorimetric comparison was made by merely putting the two tubes next to each other and looking toward the light through the column of liquid, taking care to reverse the positions of the tubes. This method of comparison, while not absolutely accurate, (as the results obtained with a Duboscq colorimeter) yet gives a very good color comparison.

In the colum "remarks" it is also seen that in some of the solutions all of the chlorides were removed at once, and in others the chlorides were removed from the entire decomposition mixture at one time, so that when aliquots were taken it was merely necessary to evaporate them to dryness. In the second case, 10 c.c. (or whatever the aliquot might be) was pipetted out of the volumetric flask containing the decomposition mixture. The alkalinity of this amount was determined by titration of an exactly equal amount of solution in a small beaker, using approximate N/10 sulphuric

acid, with phenol sulphone phthalein as the indicator. This amount of acid was then added to the original aliquot, plus a very slight excess, and the silver sulphate was added. The solution was evaporated to dryness at this point when ammoniacal silver sulphate was used, but when aqueous silver sulphate was added, the silver chloride filtered off. The solution was made alkaline with 25% sodium hydroxide, the silver oxide filtered off and the filtrate evaporated to dryness. All of the necessary quantitative precautions were taken, such as careful washing of precipitates, etc. The method was thus carried to completion.

There is no difference in the results obtained by removing all the chloride from the decomposition mixture or from aliquot portions. It is more rapid and much more convenient to remove all of the chlorides at once, altho the accuracy was found to be the same. (Table No. 68).

TABLE 68.

DETERMINATION OF CHLOROPICRIN BY NITRATE METHOD.

SODIUM PEROXIDE ABSORBING SOLUTION. 50 c.c. of Solution Used.
SATURATED SOLUTION (26 grams per 100 c.c.).

Gms. Chloropicrin Taken	Gms. Chloropicrin Found	% Decomposition	Mgm. per Liter	P.P.M.	Conc. Taken	Conc. Found	Time of Standing	Remarks
0.0158	0.01582	100.1	6.32	861	1/1160	1/1160	Over night	Duboscq Chlorine all out at once
0.0173	0.0173	100.0	6.92	942	1/1057	1/1057	"	No colorimeter Chlorine all out at once
0.0179	0.0179	100.0	7.16	975	1/1028	1/1028	"	"
0.0216	0.0216	100.0	8.64	1175	1/853	1/853	2 hr.	"
0.0310	0.0310	100.0	12.4	1689	1/592	1/592	2 "	No colorimeter Chlorine removed from 10 cc.
0.0091	0.09018	99.1	3.64	496	1/2015	1/2034	Over night	Duboscq Chlorine all out at once
0.088	0.08736	99.27	35.4	4823	1/207	1/210	"	Duboscq Chlorine removed from 3 cc.

The accuracy of the procedure was checked by nine observers as follows:

Each man weighed out a glass bulb of chloropicrin and placed the bulb into a 2½-liter bottle. The bottle was evacuated and 50 c.c. of 20% sodium peroxide were drawn in. Each observer made an analysis on an aliquot of his own solution, and then made a determination on an aliquot of every other man's solution as an unknown. Each observer know the nitrogen content of none of the solutions but his own.

The readings were all made on a Duboscq - Leitz colorimeter, and were carefully checked. (Table 69).

TABLE 64

PHENOLDISULPHURIC ACID METHOD ON UNKNOWN CONCENTRATIONS OF CHLOROPICRIN.

SODIUM PEROXIDE ABSORBING SOLUTION
20% AQUEOUS SOLUTION OF Na_2O_2

50 cc. used analysis
All stood over night.

Gms. Chloro- picrin Taken	Sol. made by	Determined by 1	2	3	4	5	6	7	8	9	Mgm. Chloro- picrin per liter	PPM.	Conc. Taken
0.0158	1	100.1	98.10	100.21	101.08	100.70	100.21	100.6	100.09		6.32	861	1/1161
0.0091	2		99.1	98.81	100.7	99.34		99.05	98.95	100.9	3.64	496	1/2015
0.088	3		99.27	99.27	97.74	98.52		98.75			35.2	4796	1/208
0.06668	4	97.15	100.09		100.39	99.47		103.0	100.89		26.68	3635	1/275
0.1226	5	99.38	93.4		98.16	100.29		104.4	99.49		49.04	6682	1/150
0.0210	6		97.5		101.12	99.27	99.72	98.25	100.15		8.4	1144	1/874
0.0102	7		99.1		95.43	98.0		100.4	100.04	97.44	4.08	555	1/1800
0.0118	8		98.5		100.0	98.98		100.3	101.31	100.0	4.72	643	1/1555
0.0357	9					100.7					14.28	1945	1/514

The sodium peroxide concentration was then reduced to 7%, 5% and 3.75%. The vacuum bottle method of decomposition was used. (Table 70).

TABLE 70.

SODIUM PEROXIDE ABSORBING SOLUTION SOLUTIONS OF VARIOUS CONCENTRATIONS. 50 c.c. of Solution used.

Gms. Chloropicrin Taken	Gms. Chloropicrin Found	Per Cent Decomposition	Mgm. Chloropicrin per L.	Parts per Million	Conc. Taken	Conc. Found	% Na_2O_2 Used
0.0173	0.01735	100.27	6.92	942	1/1060	1/1063	7
0.0192	0.01884	98.13	7.68	1046	1/955	1/973	7
0.0161	0.0163	101.24	6.44	877	1/1140	1/1125	5
0.0153	0.0154	100.65	6.12	833	1/1200	1/1200	5
0.0110	0.0107	98.3	5.5	599	1/1668	1/1772	3.75
0.0279	0.0270	100.3	10.7	1458	1/685	1/685	5

The concentration of sodium peroxide was decreased to 0.5% and 0.25%. 50 c.c. of the solution were used for the analysis in the Vacuum Bottle method (Table 71).

TABLE 71.

SODIUM PEROXIDE ABSORBING SOLUTION 50 cc.0.5% Sodium peroxide solution.

Weight Chloro-picrin Taken Gm.	Weight Chloro-picrin Found Gm.	% De-comp.	Mgm. Chloro-picrin per liter	Parts per Million	Conc. Taken	Conc. Found
0.009	0.00907	100.6	3.8	490	1/2043	1/2027
0.0136	0.01353	99.5	5.44	741	1/1351	1/1359

SODIUM PEROXIDE ABSORBING SOLUTION 50 c.c. 0.25% Sodium Peroxide Solution.

Gm. Chloro-picrin Taken	Gm. Chloro-picrin Found	% Decomposition	Mgm. Chloro-picrin per L.	Parts per Million.	Conc. Taken	Conc. Found	Remarks
0.0148	0.01413	99.5	5.92	807	1/1239	1/1298	Shaken 1 hr. constantly
0.0134	0.01331	99.1	5.36	730	1/1370	1/1380	Shaken 1 hr. Stood over night
0.0174	0.0179	104.6	6.96	948	1/1055	1/1010	Shaken 30 min. stood 30 min.
0.0255	0.0235	93.8	10.2	1390	1/719	1/766	Shaken 30 min. stood over night
0.0181	0.01763	97.4	7.14	973	1/1028	1/1053	Shaken 25 min. Stood over night
0.0119	0.01007	99.54	4.76	649	1/1541	1/1550	Shaken 30 min. stood over night

The phenol di-sulphonic acid as modified, was applied to low gas concentrations of chloropicrin. The samples of chloropicrin were drawn into a burette over mercury from a gas chamber containing a known concentration of chloropicrin. After measuring the volume of gas, the sample was transferred to evacuated $2\frac{1}{2}$-liter bottles. 50 c.c. of the sodium peroxide solution (usually $\frac{1}{4}\%$ to $\frac{1}{2}\%$) were then drawn into the bottle.

The bottle was shaken continuously for $\frac{1}{2}$ hour and allowed to stand over night and analyzed according to the procedure outlined. The results (Table 72) show that concentrations as low as 1 part in 150,000 can be determined accurately and 1 part in 200,000 can be determined with a fair degree of accuracy.

TABLE 72.

PHENOL DI-SULPHONIC ACID DETERMINATION OF LOW CONCENTRATIONS OF CHLOROPICRIN

Mgm Chloropicrin Taken	Mgm. Chloropicrin Found	Mgm. Nitrogen Taken	Mgm. Chloropicrin per Liter	Parts per Million	Concentration Taken	Concentration Found	% Decomposition	% Na_2O_2 used
2.862	2.924	0.243	1.145	155.7	1/6450	1/6320	102.1	6
2.345	2.291	0.1988	0.938	127.5	1/7874	1/8300	97.8	5
2.224	2.165	0.1895	0.8898	121.0	1/8330	1/8540	97.3	6
2.148	2.064	0.183	0.8594	116.8	1/8620	1/8920	96.2	6
1.779	1.779	0.1533	0.7196	97.8	1/10300	1/10400	98.9	1/2
1.656	1.657	0.141	0.662	89.1	1/11230	1/11100	100.0	5
1.024	1.022	0.0872	0.4096	55.7	1/18000	1/18000	99.8	2
0.9782	0.9362	0.0833	0.3912	53.2	1/18800	1/18800	100.1	1/2
0.9518	0.9915	0.0816	0.3831	52.1	1/19200	1/18800	103.5	1/2
0.938	0.97	0.0799	0.3753	51.0	1/19600	1/19230	103.4	5
0.9304	0.999	0.0792	0.372	50.6	1/19800	1/18500	107.4	1/2
0.8756	0.92	0.0746	0.3503	47.6	1/21480	1/20000	105.0	6
0.7959	0.8308	0.0678	0.3183	43.1	1/23200	1/22200	104.3	3
0.7692	0.8155	0.0655	0.3077	41.6	1/24000	1/22600	106.0	3
0.7532	0.7542	0.0641	0.3012	40.9	1/25000	1/25000	100.1	3
0.6639	0.6692	0.0565	0.2656	36.1	1/27700	1/27700	100.8	1/2
0.5997	0.6232	0.0511	0.2398	32.6	1/31200	1/30300	103.9	1/2
0.5289	0.554	0.045	0.211	28.6	1/34900	1/33300	104.6	5
0.445	0.4498	0.0379	0.178	24.2	1/41600	1/41100	101.1	1/2
0.407	0.3959	0.0346	0.162	22.1	1/45400	1/46200	97.0	1/4
0.3754	0.3686	0.0319	0.1502	20.5	1/48800	1/49500	98.5	1/2
0.3676	0.3538	0.0313	0.147	20.3	1/50000	1/51500	97.0	1/4
0.365	0.3768	0.0311	0.146	19.8	1/50500	1/50500	103.2	1/4
0.3538	0.3694	0.0301	0.1415	19.2	1/52000	1/49800	104.4	1/4
0.346	0.3626	0.0294	0.138	18.7	1/53000	1/50600	104.8	1/4
0.3359	0.318	0.0285	0.1344	18.3	1/54600	1/58100	97.4	1/4
0.328	0.334	0.0278	0.131	17.8	1/56000	1/55500	102.0	1/4
0.3283	0.3261	0.0279	0.131	17.8	1/56000	1/56270	101.17	1/4
0.3267	0.3268	0.0276	0.1306	17.6	1/56800	1/58000	96.9	1/4
0.3119	0.3252	0.0265	0.1248	16.4	1/60900	1/56200	104.2	1/4
0.2613	0.2533	0.0222	0.104	14.2	1/71300	1/72000	97.0	1/4

TABLE 72 (cont'd).

PHENOL DI-SULPHONIC ACID DETERMINATION OF LOW CONCENTRATIONS OF CHLOROPICRIN
(Cont'd)

Mgm. Chloropicrin Taken	Mgm. Chloropicrin Found	Mgm. Nitrogen Taken	Mgm. Chloropicrin per Liter	Parts per Million	Concentration Taken	Concentration Found	% Decomposition	% Na_2O_2 used
0.2387	0.2408	0.0203	0.0954	13.0	1/76000	1/76300	100.8	1/4
0.241	0.242	0.0205	0.0964	13.1	1/76300	1/76300	100.0	1/4
0.2248	0.2367	0.019	0.0899	12.2	1/81600	1/77500	105.2	1/4
0.2207	0.2337	0.0186	0.0882	12.0	1/83100	1/78500	106.0	1/4
0.210	0.2088	0.0178	0.084	11.4	1/87300	1/88500	98.6	1/4
0.2042	0.194	0.0174	0.0816	11.1	1/89800	1/94500	95.0	1/4
0.1898	0.1854	0.0161	0.0759	10.3	1/97100	1/99000	97.7	1/2
0.1986	0.1986	0.0169	0.0794	10.8	1/100000	1/100000	100.0	1/4
0.1834	0.1677	0.0154	0.0733	9.9	1/101000	1/109000	92.0	1/4
0.1756	0.1867	0.1496	0.0702	9.6	1/105000	1/100000	105.0	1/4
0.1721	0.1724	0.0146	0.0688	9.2	1/108600	1/108600	100.1	1/4
0.1679	0.1690	0.0142	0.0671	9.1	1/109300	1/108570	100.8	1/4
0.1607	0.1478	0.0136	0.0643	8.8	1/113600	1/123500	93.0	1/4
0.1606	0.1596	0.0154	0.0642	8.7	1/114300	1/114900	99.8	1/4
0.1572	0.1636	0.0135	0.0629	8.5	1/117600	1/113600	104.0	1/4
0.1493	0.1467	0.0123	0.0597	8.1	1/122500	1/125000	98.0	1/4
0.1497	0.1525	0.0126	0.0598	8.1	1/123000	1/120300	102.0	1/4
0.1274	0.1219	0.0108	0.0509	6.9	1/144900	1/151000	95.7	1/4
0.1267	0.1216	0.0107	0.0506	6.8	1/147000	1/151000	96.0	1/2
0.1014	0.0985	0.0086	0.0405	5.5	1/181800	1/186000	97.1	1/4
0.0952	0.1126	0.0081	0.0381	5.1	1/196000	1/186800	105.0	1/4
0.0933	0.0953	0.0079	0.0373	5.0	1/197600	1/195000	102.0	1/4
0.0918	0.1079	0.0078	0.0367	5.0	1/204000	1/172000	109.0	1/2
0.091	0.0947	0.0077	0.0364	4.9	1/204000	1/196000	104.1	1/4
0.0872	0.0875	0.0074	0.0348	4.7	1/211400	1/210000	100.3	1/4
0.0792	0.0876	0.0067	0.0316	4.2	1/233000	1/210000	110.0	1/4
0.075	0.084	0.0063	0.0300	4.0	1/245000	1/218500	112.0	1/2
0.0677	0.0607	0.0057	0.027	3.6	1/310000	1/345500	89.7	1/2

Oxidation of Chloropicrin by Hydrogen Peroxide Determination of Nitrogen.

While the work on strong solutions of sodium peroxide was being conducted, the first difficulty which had to be remedied in the phenol di-sulphonic acid was the large residue remaining on evaporating the aliquot. The use of hydrogen peroxide suggested itself and if satisfactory would avoid any residue coming from the peroxide. The 3% hydrogen peroxide was used, but an objection to its use was the high chloride content. It was necessary to use such a volume of the hydrogen peroxide that a high chloride blank was always obtained.

The Phenol di-sulphonic acid method as outlined was used. The results are satisfactory and show that the method may be used with good results. The 2 1/2 liter Vacuum Bottle method was used to decompose the chloropicrin.

TABLE 73.

Hydrogen Peroxide absorbing Solution
125 cc. Hydrogen Peroxide (3%) in 15 cc. of 10% Alcoholic Sodium Hydroxide.

Gm. Chloropicrin Taken	Gm. Chloropicrin Found	Per cent Decomposition	Mgm. Chloropicrin per liter	Parts per million	Concentration taken	Concentration found
0.0097	0.00957	98.62	3.88	528	1/1891	1/1919
0.0049	0.00488	99.6	1.96	668	1/1497	1/1504
0.0302	0.0293	97.1	12.08	1646	1/608	1/626
0.0531	0.0547	103.0	21.24	2894	1/345	1/335

Colorimetric Determination of Trinitrotoluene.

For the oxidation of the trinitrotoluene a 5% aqueous solution of sodium peroxide was used. In the cold the reaction was rather slow and it required about 36 hours to dissolve the trinitrotoluene. On warming the speed of reaction was greatly increased. The solutions obtained were colored light yellow and could probably be compared quantitatively with a standard trinitrotoluene solution. This was not studied any further. An aliquot was taken in a porcelain evaporating dish, evaporated to dryness, treated with 2 cubic centimeters of phenol di-sulphonic acid. This was washed into a Nessler tube and diluted to 40 cc. and made up to the 50 cc. mark with concentrated ammonium hydroxide. Readings were made with Duboscq colorimeter using a standard similarly prepared from sodium nitrate for comparison. A blank determination was made along with the determination.

RESULTS

TABLE 74.

T.N.T. taken Cm.	cc. of 5% Na_2O_2 used.	T.N.T. found Gm.	Percent found
0.0133	10	0.0132	99.25
0.0112	10	0.0116	103.57
0.0103	10	0.01092	101.10

Determination of a Mixture of Chloropicrin and Trichlormethylchlorformate (Superpalite) with Sodium Peroxide.

The method for the determination of a mixture of chloropicrin and Superpalite depends on the oxidation and decomposition of these compounds by means of an aqueous solution of sodium peroxide. A single sample only is necessary whether the Direct or Vacuum Bottle method of decomposition is used. An aliquot is used for the determination of the sodium nitrate formed by the oxidation of chloropicrin by the phenol di-sulphonic acid method. Another aliquot is used for the determination of the total chlorides. The chloride due to chloropicrin is deducted from the total chloride, and the result is expressed as superpalite. Concentrations of the gaseous mixtures were used, and the amount of each component was varied from 30% to 70%. The results obtained for both chloropicrin and superpalite were as accurate in the various mixtures as when the sodium peroxide method is used on each component.

Experimental.

Samples of the mixture were collected in evacuated 2 1/2 liter bottles. 50 cc. of 1% solution of sodium peroxide were introduced into the bottles. The bottles were shaken 15 minutes on the wheel and allowed to stand overnight. The contents of the bottles were then transferred to volumetric flasks and an aliquot taken for the total chloride determination.

Total Chloride.

The standard sodium peroxide method was used for the determination of toal chloride.

Determination of Chloropicrin as the Nitrate.

The phenol di-sulphonic acid method was used for the determination of the nitrate present. Blank determinations were made at the same time.

The chloride due to chloropicrin was calculated from the equation.

14:01 : 3(35.46) :: Wt. of Nitrogen found : X.

The value of X. subtracted from the total chloride found, divided by the theoretical amount of chloride present in the Superpalite taken gives the per cent of Superpalite found.

TABLE 75.

Determination of Mixture of Chloropicrin and Superpalite

50 cc. 1% Sodium Peroxide solution.

Time Shaken, 10-15 minutes.

Time Standing - Overnight.

Mgm. Chloropicrin Taken	Mgm. Chloropicrin per L.	Conc. Taken	Mgm. Superpalite Taken	Mg. Superpalite per L.	Conc. Taken	Composition mixture		% of Total Cl Found	% Chlorpicrin Found	% Superpalite Found by Diff.
						Chlor.	Super.			
8.7	3.472	1/228	8.1	3.240	1/308	52	48	101.53	99.97	102.5
8.7	3.472	1/228	7.3	2.912	1/344	54	46	100.08	100.54	99.5
5.5	2.212	1/452	7.5	2.980	1/335	42	58	102.10	104.11	101.4
6.3	2.50	1/400	8.3	3.32	1/301	43	57	100.22	96.34	102.8

SUMMARY.

The use of sodium peroxide for the determination of nitro-groups in organic compounds by modifying the phenol di-sulphonic acid method, when chlorides are present, gave accurate results on chloropicrin and Trinitrotoluene. The determination was very accurate for 1 part of chloropicrin in 150,000 of air. The method was then extended to the analysis of a mixture of chloropicrin and trichloro methyl chloroformate in low concentrations with good results.

The use of sodium peroxide may be extended to the determination of other nitro compounds, and if satisfactory, should make this method a desirable one to use in Organic Analysis.

III. SAMPLING OF GAS CONCENTRATIONS.

III. SAMPLING OF GAS CONCENTRATIONS.

The sampling of gases in the experimental study of gas concentrations is a very important problem. The collection of samples must be carried out with several purposes in mind. The method used depends largely on the conditions of the experiment and the purpose of conducting it. The term gas as used includes not only substances which are gases at ordinary temperatures, but also liquids of high and low vapor pressure, as well as solids. In producing a concentration of a liquid and solid, the use of a detonator produces a vapor or finely atomized spray condition of the liquid as well as a gaseous phase, and a very finely divided particulate phase of the solid. Sampling concentrations of this nature requires the use of special apparatus.

It is necessary to know the rate of drift of the gas cloud, its depth, its breadth and the distance the effective concentration will travel. The sampling is carried out in the open, in trenches and dugouts. During artillery fire from a battery of guns, samples are collected at the target. Hand sampling under these conditions is impossible. In static trials, hand sampling is possible in the trenches with proper precautions. For artillery fire tests it is necessary to use a safe method of sampling which is accurate and efficient.

Taking gas samples under field conditions requires care and accuracy. The sample must be collected in such a manner that all the data regarding that sample may be absolutely obtained: for example, the volume of the sample bottle, the exact time at which the sample was taken, the concentration of gas in the sample bottle representing the concentration of that position at the time when that sample was taken, and exact location of the position in which the sample was taken must all be carefully recorded. When the gas cloud is moving quickly a container must be used that will be filled almost immediately after the necessary step has been taken to obtain the sample. The evacuated bottle fulfills these conditions as completely as it is possible to control them in the field. For lower concentrations the size of the bottle may be increased. When the concentrations are very low, an Average sample gives the best results.

The methods of sampling and the types of Apparatus used for the collection and handling of samples in experimental work are here described. The apparatus was used on concentrations of substances containing either a halogen or a nitrogen, and the analysis was made for [illegible] of these elements. The wide application which can be made of these methods of sampling and apparatus makes it desirable to describe them somewhat in detail.

Three types of sampling device were used. Two were automatic, being electrically operated, and the third was hand operated.

1. The Automatic Electrical Gas Sampler, fitted with an evacuated bottle and an electrical magnet, gives an instantaneous sample when the magnet functions.

2. The Automatic Average Gas Sampler is equipped with three copper cylinders. An opening at the bottom of each cylinder is closed by an electrical magnet. The cylinders are filled with water. The opening at the top is connected with a set of absorption bottles. When the magnet functions, the water in the cylinder runs out and an equal volume of air is aspirated through the absoprtion bottles. The size of the copper cylinders used may be varied in size to meet the conditions. The size of the opening at the bottom determines the length of time in which the coppercylinder will empty.

3. The Hand Gas Sampling Pump may be used to give an average and a continuous sample. The Pump consists of the tank, drum and two-way valve. The drum may be drawn up and let down in the Tank much like a piston. A water seal between the tank and drum makes the connection air tight. An absorption bottle is fastened to the two-way valve. As the drum is drawn up, an equal volume of air is aspirated through the absorption bottle, the two-way valve and into the drum and is held there by the water seal. The air is allowed to escape by turning the two-way valve and lowering the drum.

The evacuated gas sample bottle in the Automatic Electrical Gas Sampler, was used with greater ease and rapidity than the other two types of apparatus. A large number of

samples could easily be collected in this manner and transported from the field to the laboratory. The evacuated sample bottle is especially desirable where the concentration is rapidly dispersing. Concentrations produced from liquids and solids must be taken instantaneously at the desired time as the maximum concentration is maintained but a very short time. An Average Sample usually compares favorably with the mean of a series of instantaneous samples at a given position.

AUTOMATIC ELECTRICAL GAS SAMPLER.

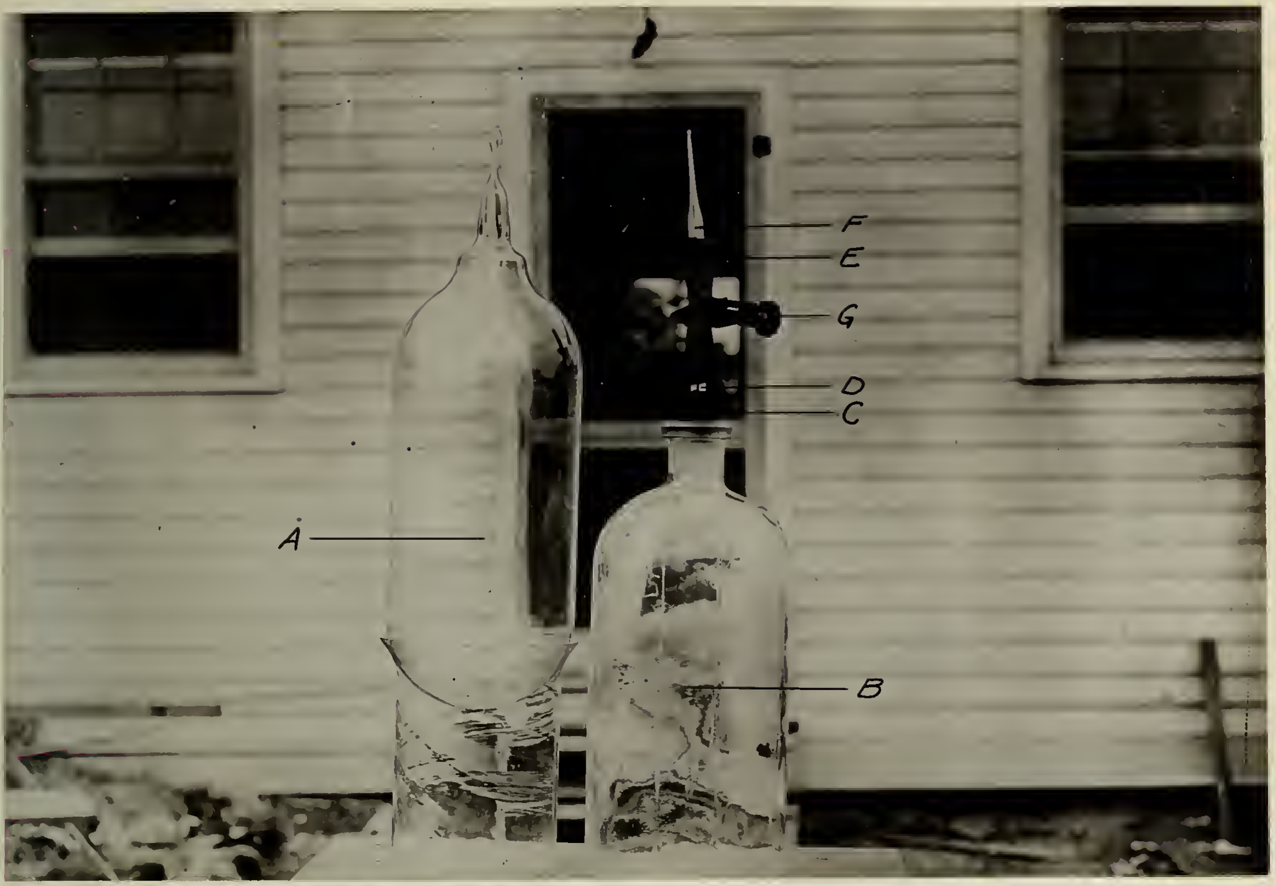
The apparatus consists essentially of the evacuated sample bottle, the sample bottle box, the electrical magnet and coil, the magnet support and the electrical connections with the keyboard at the observation tower.

(A) Sample Bottles.

Several types of Vacuum bottles were used varying from 2½ to 3 liters in capacity. The Lakehurst Proving Ground Vacuum Bottle was also made with a capacity of 5 liters. Vacuum bottles sealed off at evacuation were very convenient due to the fact that they were alwaysready for use and the pressure remained constant. Bottles fitted with rubber stoppers were also used, but were always evacuated just prior to using.

The Nela bulb (A. Photograph No. 1) is a round bottom bottle having a capacity of 2½ liters and weighs 8 ounces. It fits snugly into the sample box. A Nela Lamp Works Apparatus for evacuating electric light bulbs is used to evacuate and seal off the bulbs. A large vacuum pump reduces the pressure to about 20 mm. and the pressure is reduced to 1 to 5 mm. by multiple vacuum pumps. The Nela bulb is ready for use at any time and retains its original pressure. The bulb may be used over again and again by sealing a new glass tip on the bulb and re-evacuating it.

The Nela bulb was too fragile for constant field usage. It was found that a strain was developed in the glass



PHOTOGRAPH NO. 1

due to the process of manufacture or of evacuation, with subsequent cracking of the bulb when the vacuum was released. The round bottom of the bulb always made it necessary to support the bottle.

The second type of sample bottle is the ordinary 2½ liter acid bottle with the ground neck (B Photograph No. 1).

This sample bottle consists of the bottle proper, the special size No. 23 rubber stopper (c), glass connection tube (d), heavy pressure tubing (e), glass capillary tip (f), and the special brass screw clamp (g).

The glass tubing has a 2 mm. wall, and an outside diameter of 10 mm. which insures a very tight connection between the glass and the rubber tubing. The tip is made from the same kind of glass tubing. Various forms of tips may be used, depending on whether a single, duplicate or triplicate sample is desired. The set up for a single sample is shown in Photograph No. 3, 4 and 5, and for a duplicate sample in Photograph No. 6. For triplicate samples a cross tip is used instead of the T tip in duplicate samples.

The Nela bulb could only be used for taking single samples. The 2½ liter acid bottle was easily adapted for duplicate samples. The disadvantage of the Acid bottle was in the fact that it had to be evacuated just before using. The stopper was always inserted by means of an especially designed Stopper Holder, which inserted the stoppers much more securely than it was possible to do by hand. In spite of this fact there was always some leakage after four hours. After the sample had been collected in the field and the

PHOTOGRAPH NO. 2

pressure in the bottle was atmospheric, it was found that during transportation to the laboratory a stopper might become loosened unless a clamp to hold the stopper in the bottle was used.

The L. P. G. Vacuum Bottle (Photograph No. 2) includes the good points of the first two bottles with as few of their disadvantages as possible. This bottle weighs about 700 grams and is made with a capacity of 2½ to 5 liters. It is made of extra heavy lime soda glass and is carefully tempered. In the process of tempering, the temperature is kept at 1800° - 1900° Fahrenheit for twelve hours, and then slowly cooled over the same period of time. As blown in the mold the neck of the bottle is made in two sizes. The second or smaller size is drawn down with a gaffering tool to a quarter inch bore with a ring finish. The bottom of the bottle is somewhat concave, making it stronger for evacuation purposes and allows the bottle to stand unsupported.

A glass tip may be sealed on the L. P. G. bottle and it may then be evacuated and sealed off as is done with the Nela bulb (2, Photograph No. 2). The bottle may be stored and used at any time. The ring neck shown in bottle No. 1 photograph No. 2 may be left on and a piece of rubber tubing slipped over the ring, and fitted with a tubing clamp and a glass tip. (3 Photograph No. 2). Only a very small portion of the rubber tubing beneath the clamp is in contact with the gas sample. The bore of the neck of the L. P. G. Vacuum Bottle is so small that the chemical action of the gas on the

rubber is negligible. The rubber stopper of the 2½ liter bottle is eliminated, with very good results; in the 2½ liter acid bottle a constant source of trouble is the necessity of having the stoppers fit tight. The L. P. G. Vacuum Bottle can be used for duplicate samples with better success than the 2½ liter acid bottle. The L. P. G. Vacuum Duplicate Bottle has no stopper to adjust and the side arm is sealed directly on it, whereas in the acid bottle it is inserted through a rubber stopper. By eliminating several rubber connections the L.P.G. showed marked advantages over any other bottle. (4 Photograph No. 2). It has been shown in tests that the arrangement with the rubber tubing over the ring neck (3 Photograph No. 2) retains its vacuum as well for 36 hours as it does for 10 minutes.

(B) Sample Bottle Box.

The box is made of hard wood (See Photograph No. 3, 4, 5) having an inside diameter of 5" and walls of 7/8" material. The box is 15" high (See Plate No. 11). For duplicate samples, an arrangement as shown in (5 Photograph No. 6) is used. The sample box is equipped with two thumb screws (H, Photograph No. 4) placed 5" apart, for the purpose of holding the magnet support. Two 1/4" slots are cut into the box into which are passed the thumb screws (K) for holding the cover. The two shaped stake holders (L) Photograph 3 and 4) are screwed into one side orend of the box, through which a stake may be driven to hold the box in a horizontal or vertical position. The cover of the box

(M, Photograph 5) fits over the top of the box and holds the bottle in place and also prevents breakage from shell fragments.

The horizontal sampler may be used where the boxes may be put on shelves in trenches, etc. In the open or on the ground, the vertical sampler must be used. The arrangement of the Magnet Support is the only difference between the Vertical and Horizontal Sampler.

(C) Magnet Support.

The form of magnet support (N Photograph No. 3 and 4) varies with the vertical and horizontal type. The dimensions of the vertical magnet support are given in Plate No. 1, the dimensions of the horizontal support are identical. The magnet support contains a slot (O, Photograph 4), through which the thumb screws (H) on the sample bottle box pass; this allows for the necessary adjustment due to irregularity of tip lengths, etc. and also allows the magnet support to be easily shifted to one side to replace a bottle that has been used. Projecting from the magnet support is the glass tip clamp (P, Photograph 3 and 4). The glass tip is run through the hole (Q, Photograph No. 5) and the clamp is tightened by means of the thumb screw (R, Photograph No. 4). The curved block (S, Photograph No. 4) on the vertical magnet support serves as a pulley over which the chain slides after the weight has fallen from the hook. Photographs Nos. 3, 4, 5, and 6 fully illustrate the support. The electrical binding posts T are shown on all of the Photographs.

Electrical Magnet and Coil.[1]

The magnet and coil are fastened to a casting (U, Photograph No. 3), this in turn is fastened to the magnet support. (Photograph 3, 4, and 6 and Plate No. 1 and 2). In an ordinary field experiment, six storage batteries are used, furnishing 36 volts. The current enters the binding post at T, (Photograph No. 3) and passes to the connection at W. This connection is insulated from the casting U. The current then passes through the spring circuit breaker X and through the soft iron bar Y (which is hinged), also through the casting U, then through a lead around the coils and back to the remaining binding post. The current passing around the coil magnetizes the core, which draws the soft iron bar to it, permitting the lead weight of 0.45 kilogram to slip off the hook (2) and thus break the tip of the bottle. To the weight is attached a brass chain fitted with a small copper cap (3), which fits snugly over the end of the glass tip, and makes a clean break when the weight is released. With a small file, a scratch is made on the glass tip, and in this way the breaking of the tip is controlled. The small circuit breaker prevents the passage and waste of current after the weight has dropped, by breaking the circuit between the arm (4) and soft iron bar (Y, Photograph No. 3) and Plate No. 2. By means of the circuit breaker one can immediately see whether or not a given magnet has functioned properly.

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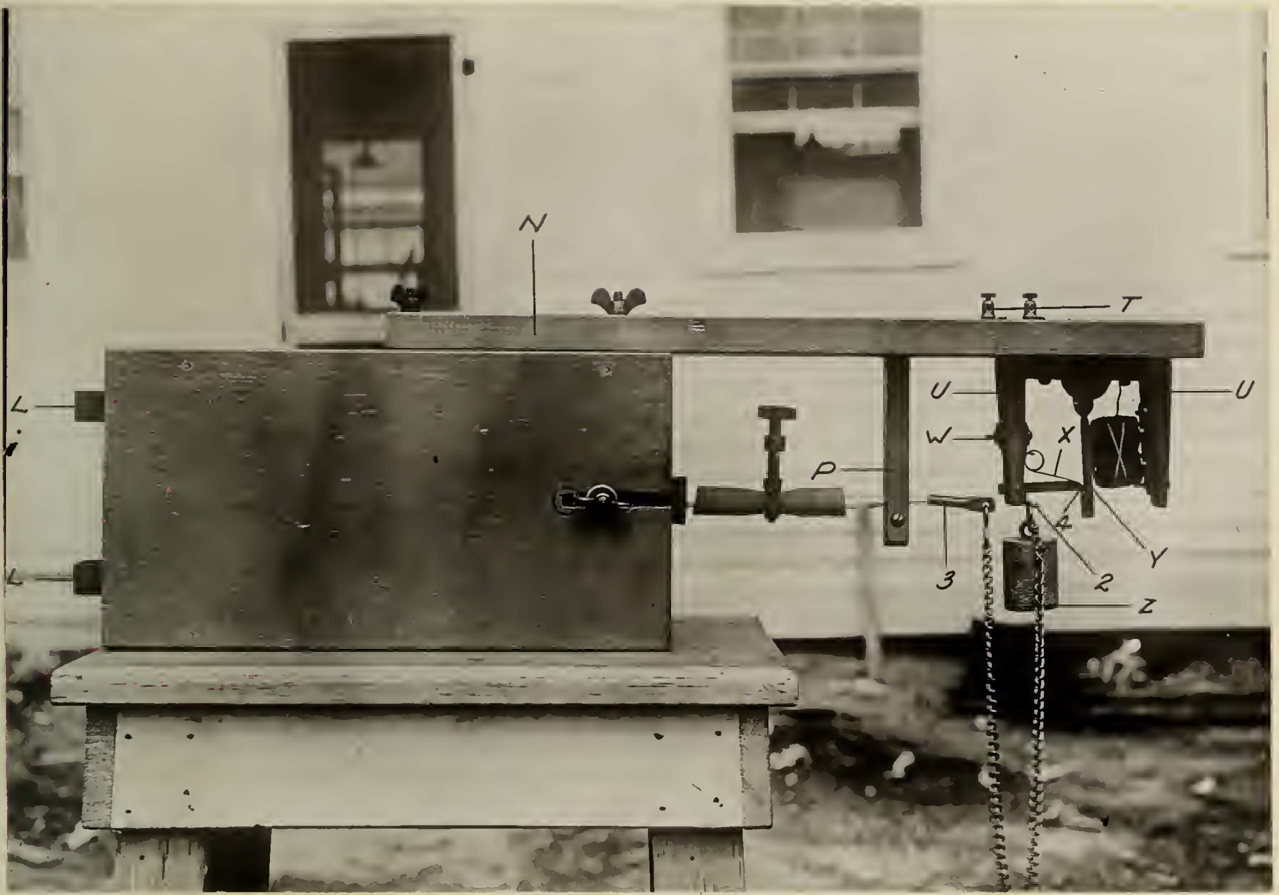
[1] The Electromagnet was designed by Wm. S. Bacon.

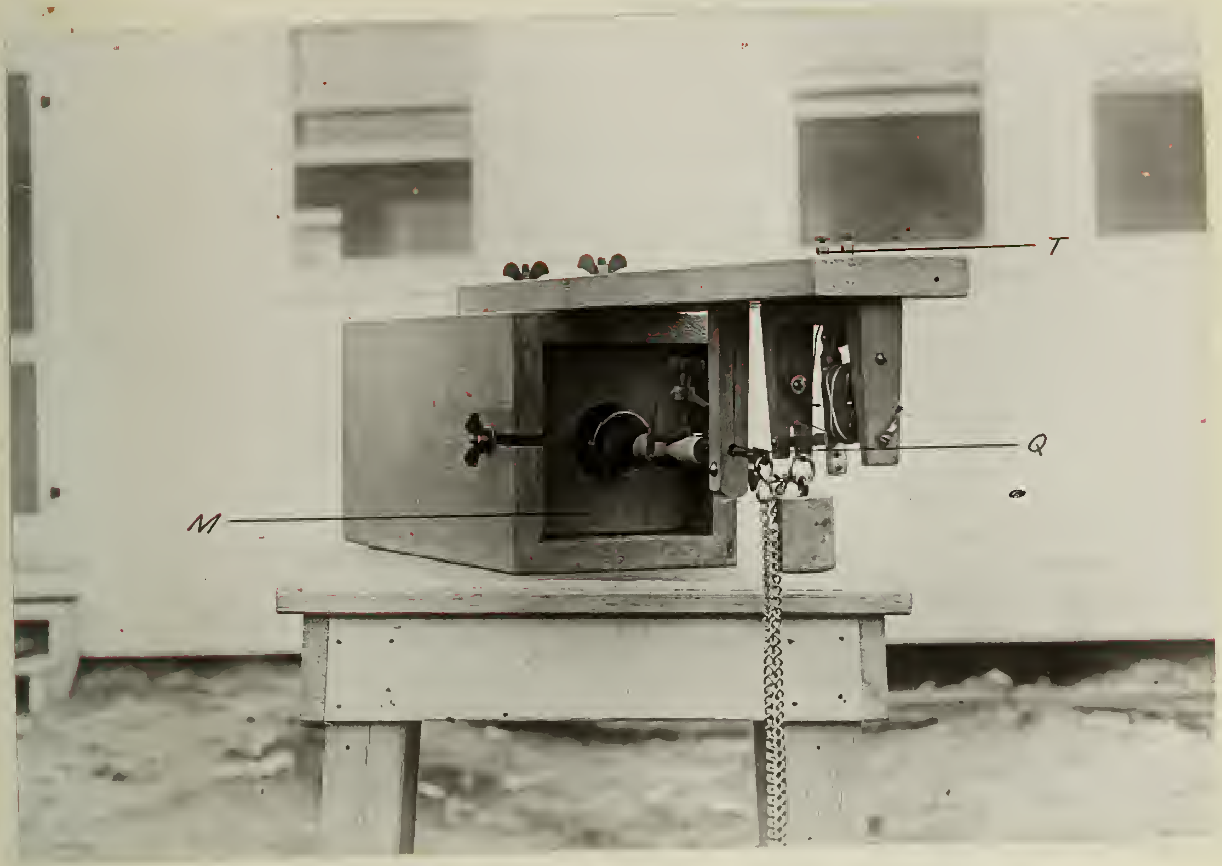
As soon as the magnet has functioned the circuit breaker breaks connection and allows no more current to pass through.

Electrical Connections, Keyboard, etc.

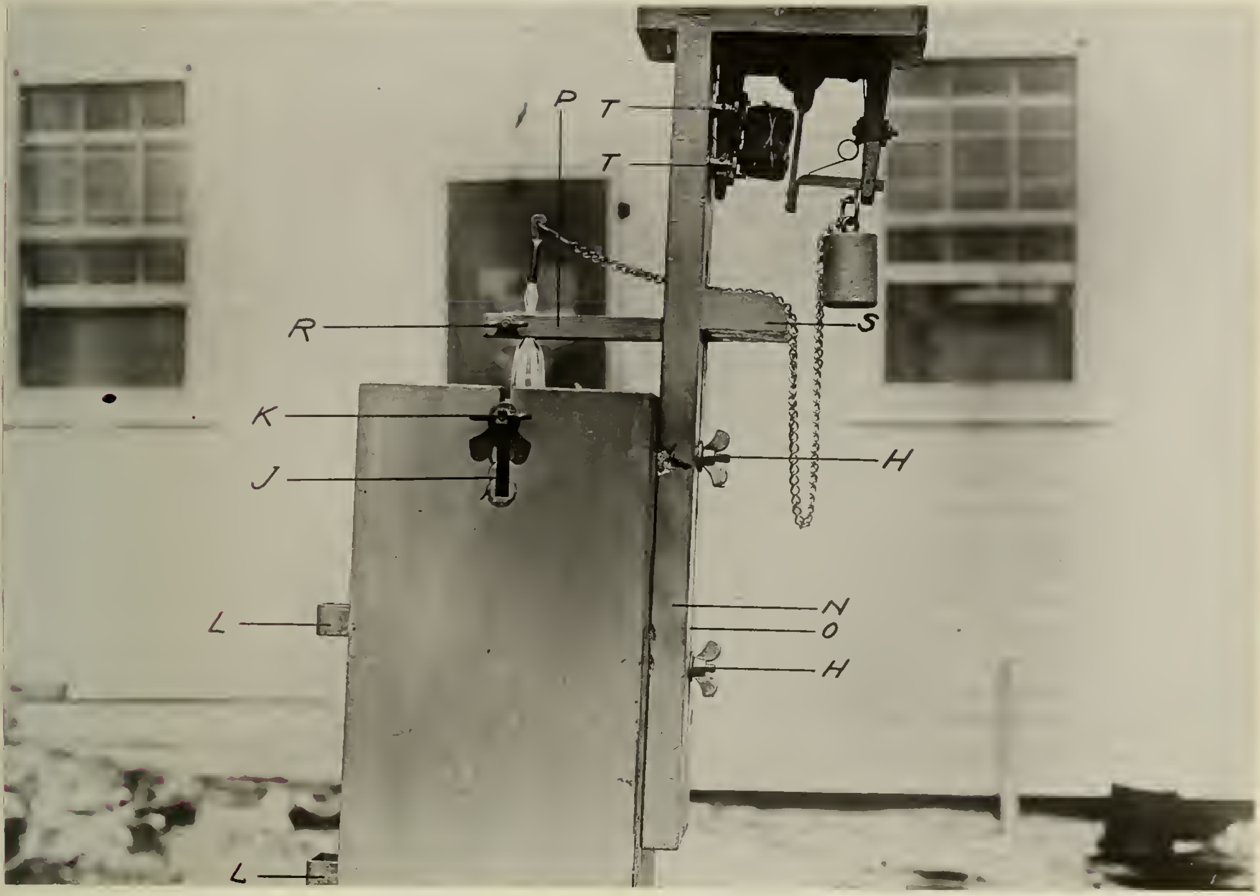
The trench system used for experimental work was a reproduction of sections of trenches. The trench was provided with one shelf two feet from the trench floor, and another four feet from the floor upon which the horizontal type of sampling apparatus was used. The parapet of the trench was from six to seven feet from the trench floor and the vertical sampling apparatus was used here as well as in the open. Each yard of the trench was provided with electrical connections having a separate lead to the keyboard in the observation tower which was located about 150 yards from the trench. By pressing the button on the keyboard for a certain position, the circuit was closed, causing the weight to fall. The tip was thus broken off the bottle and the gas and air were permitted to enter. The keyboard was so arranged that any number of individual samples could be taken whenever desired by pressing the correct buttons, though the use of a common switch made it possible to take all the samples at once. The circuit was always previously tested by a small ammeter on the keyboard which showed whether the circuit breaker was making proper contact with the bar of the magnet. The current used in the ammeter to test the circuit was too small to magnetize the core and cause the weight to fall. As soon as the sample had been taken the ammeter was again used to see if the magnet had functioned.



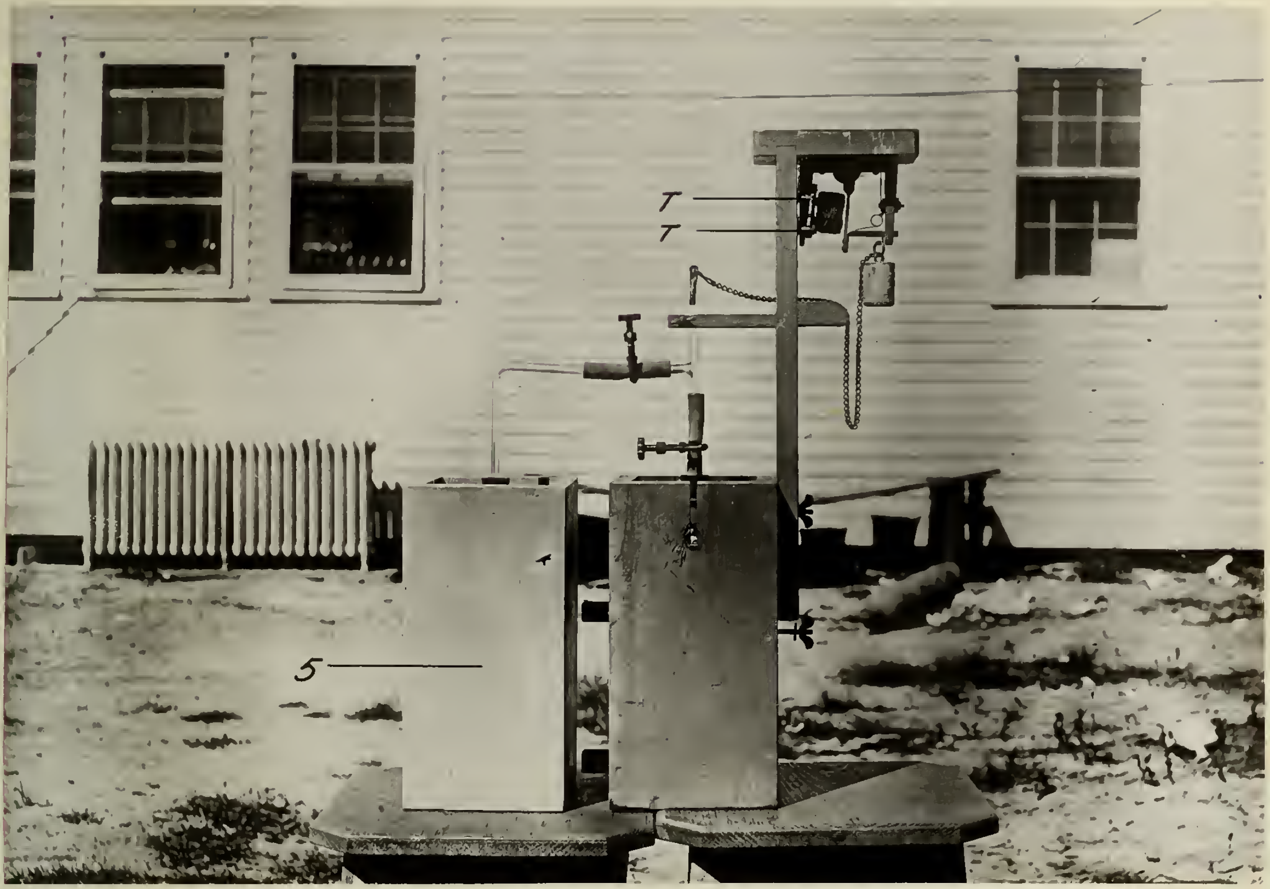
PHOTOGRAPH NO.3



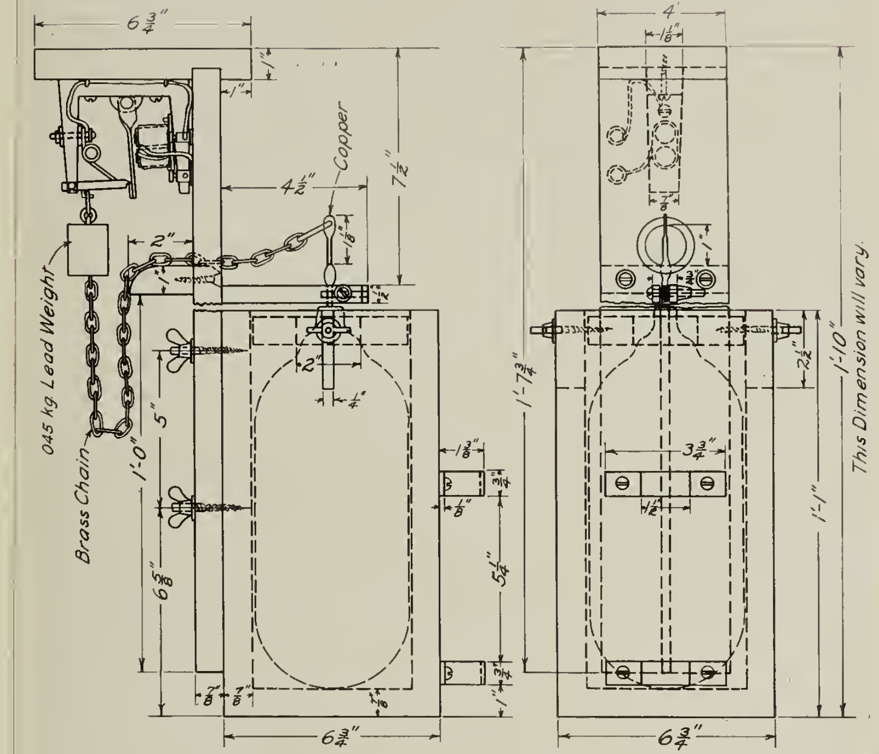
PHOTOGRAPH NO.4



PHOTOGRAPH NO.5

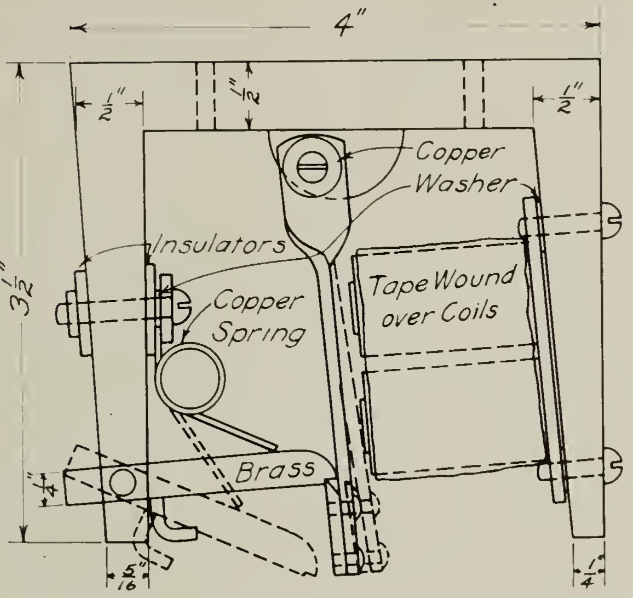


PHOTOGRAPH NO. 6



Automatic Electrical Gas Sampling Apparatus
Vertical Type

PLATE NO. I



Magnet for Automatic Electrical
Gas Sampling Apparatus
(Vertical Type)

PLATE NO. 2

PROCEDURE FOR GAS SAMPLING UNDER FIELD CONDITIONS.

The L. P. G. Vacuum Bottle with rubber tubingconnection (3, Photograph No. 2) or the 2½ liter acid bottle are evacuated to 15 - 25 millimeter pressure. The tubing clamp is then tightened and the glass tip, drawn out and sealed at one end, is inserted into the rubber tubing. The bottles are fitted with the desired glass tip, depending on the nature of the experiment, whether single, duplicate or triplicate samples are to be taken. The L. P. G. Vacuum bottle (2, Photograph 2) fitted with the glass tip and sealed off during evacuation may also be used. The pressure in each bottle and its capacity are recorded as part of the data.

The bottles, sample boxes and other equipment are taken to the trenches and placed in the desired sector of the trench. The boxes are placed on the shelves, and the bottles placed in them. If duplicate samples are to be collected, the bottles are fastened together and the magnets are attached to the boxes. The electrical connections having been made and tested, the tubing clamps are released. The glass tip on each bottle is lightly scratched with a file. The weights are hung on the hook of the magnet and the copper cap is placed over the glass tip.

A final inspection should show the circuit breaker above the bar of the magnet in each case and all connections properly made. A record of the number of each bottle and exact location in the trench or in the open is taken.

During artillery fire on the trench, samples are taken when observations at the tower show the best gas wave. The time of sampling is recorded. After cessation of firing, the tubing clamps are closed. 10 - 15 minutes usually elapses between the fall of the last shell and closing of the last bottle. It is assumed that the diffusion through the capillary of the broken tip during this time interval is negligible. After dismantling the apparatus, the bottles are returned to the laboratory. The absorbing solution is introduced by means of the Lakehurst Proving Ground (L.P.G.) Filler, designed for this purpose. The bottles are shaken on the shaking wheel for one-half hour and immediately analyzed or preferably allowed to stand a few hours before analysis. As an alternative the bottles may be thoroughly shaken and allowed to stand over night before proceeding with the analysis.

The L.P.G. Filler.

The introduction of 50 cc. of absorbing solution to a bottle containing the sample of any gas must be done without loss of the gas in the displaced air-gas mixture. The L.P.G. Filler introduces the absorbing solution without loss of any displaced gas and makes it possible to introduce the absorbing solution quantitatively. It is possible to handle a large number of samples quickly and efficiently by using the Filler. The Filler is made in two designs and both have been used daily for six months with very satisfactory results.

Description.

The two types of Fillers are of the same dimensions,

both working similarly and equally well. The Filler illustrated in Fig. 1, Photograph No. 7, depends upon the siphon (F) to draw the solution into the bottle. The Filler in Fig. 2, has a coil (G) which draws the solution into the bottle. The broken tip is removed from the bottle and the Filler is inserted (Photograph No. 8). The absorbent is poured into the funnel (A), and part of it flows directly into the bottle. The pressure of the displaced air causes some of the absorbent to rise in bulb (B) and almost fill it. The displaced air bubbles through the absorbent in (B) and the gas present in the air-gas mixture is absorbed. The Filler is so made that the bulb (B) will always contain some absorbent until the necessary amount of air has been displaced. The bulb (A) empties very quickly, but the tubing is filled until bulb (B) is empty. The displaced air always passes through bulb (B), which contains absorbent as long as any air is passing out. The reason for its going to the sidearm at (B) rather than at (A) is due to the fact that (B) is the shorter arm, and has the lower water level, and hence offers the less frictional resistance. The L.P.G. Filler will take the absorbent very quickly, although it is best not to let the bulb (B) fill up too high because the air bubbling through the absorbent too quickly causes splashing into the spiral (E). To prevent loss of any absorbent due to violent bubbling of the air, the bulb (B) is fitted with a spiral (E).

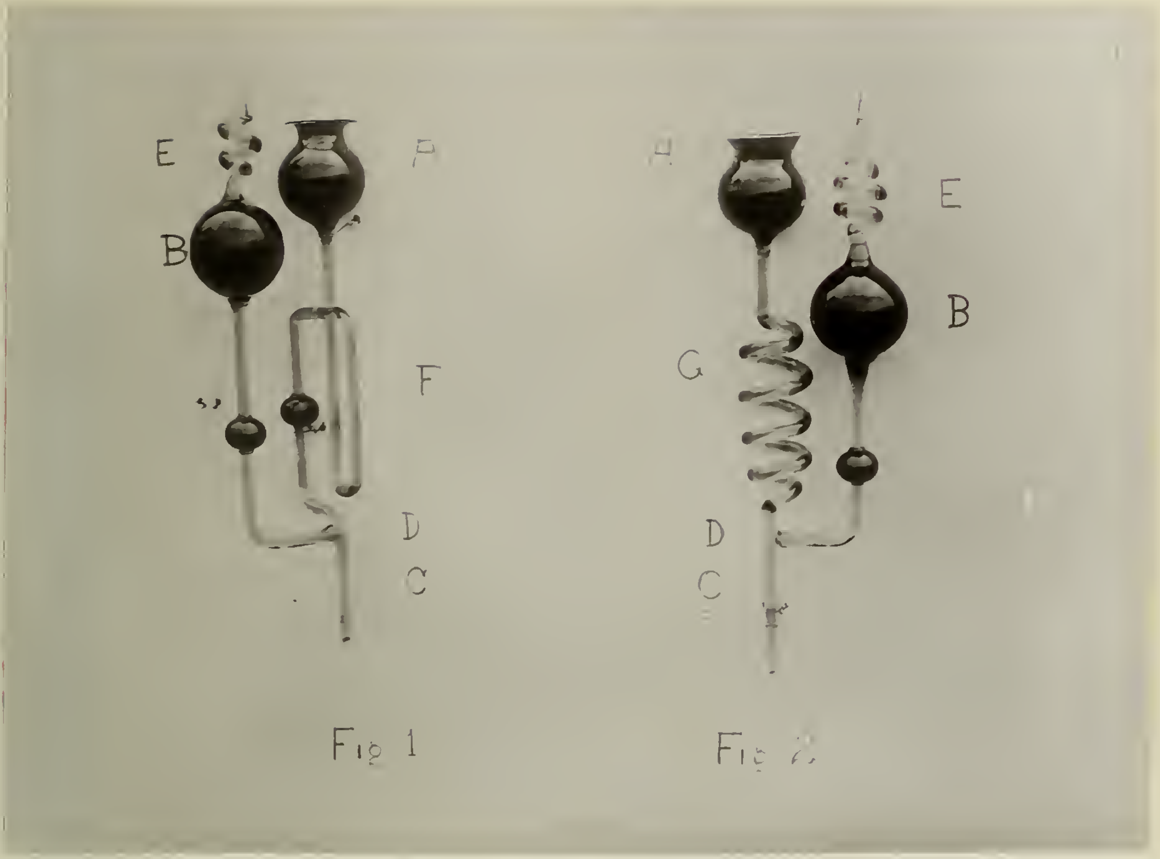
Dimensions of the L.P.G. Filler.

The total length from top of bulb (A) to end of

tube (C) is 23 cm. The distance from bottom of bulb (A) to end of tube (C) is 18 cm., making the length of the bulb (A) from the top to point of connection with the side-arm 5 cm. The diameter of (A) is 45 mm., while the diameter of the smaller bulbs is 20 mm. It is 14 cm. from the bottom of (A) to the connection at (D). The top of bulb (B) is almost in line with the bottom of bulb (A), the side-arm being 14 cm. long.

The siphon (F), and coil (G), are each 9 cm. long. The side-arm of bulb (B) is 4 cm. from the side-arm of bulb (B).

The coil (G) has 5 turns, while the spiral (E) may have 2 or 3 turns. The opening of spiral (E) is about 2 mm. in diameter. 7 mm. tubing is used in making the apparatus.



PHOTOGRAPH NO. 7

PHOTOGRAPH NO. 8

To show that the L.P.G. Filler introduces the absorbing solution into the bottle quantitatively or within experimental error, several experiments were conducted. Absorbing solutions containing high and low amount of chloride were introduced into 2½ liter sample bottles, containing air with the L.P.G. Filler in the same manner in which it is used to introduce the absorbing solutions into a large number of sample bottles. In view of the fact that most all the gases used contained halogen, any loss of absorbing solution while introducing it into the bottle would represent a loss of chloride, and would be calculated as so much gas. Thus giving a higher concentration of the gas than was actually present. The experiments conducted show that the Filler is accurate and efficient. Titrations of absorbing solutions introduced with the Filler checked closely with aliquots of the absorbing solutions measured directly into an Erlenmeyer flask. The results show that even with a solution of 3% sodium hydroxide as the absorbent, which has a high chloride content, the results are within experimental error. It is safe to conclude that the error due to variation in the volume of absorbent introduced into the sample bottle by means of the Filler is negligible. Three solutions were used, sodium hydroxide, sodium sulphite and sodium peroxide. Of these thefirst is very high while the last is very low in chloride content.

3% Sodium Hydroxide Solution.

A 3% solution of sodium hydroxide was prepared. A 50 cc. portion (Sample B) was measured out into an Erlenmeyer

flask. Other 50 cc. portions (Samples 1-5) were introduced into 2½ liter acid bottles through the Filler. The solutions were transferred to Erlenmeyer flasks, and the chlorides determined by the Volhard Method using N/100 solutions.

3% AQUEOUS SODIUM HYDROXIDE ABSORBENT.

No.	CC. of N/100 A_gNO_3	CC. of N/100 NaCNS	CC. of N/100 A_gNO_3 Needed to PPt. Chlorides in NaCH	Difference Between Blank & Samples Intro. thru L.P.G. Filler
B.	15.78	7.98	7.80	
1	15.78	7.64	8.14	-0.34 cc.
2	15.78	8.46	7.32	-0.48
3	15.78	8.08	7.70	-0.10
4	15.78	8.28	7.50	-0.30
5	15.79	8.03	7.75	-0.05

ALCOHOLIC SODIUM SULPHITE ABSORBENT.

A 3% alcoholic sodium sulphite solution (3% Na_2SO_3 in 30% alcohol), was used as the absorbing solution. 50 cc. of this solution was introduced into the 2½ liter sample bottle by means of the L.P.G. Filler. The contents of the bottle was then washed into Erlenmeyer flasks and the chlorides were determined by the Volhard Method, using N/100 solutions.

Another 50 cc. (B) was introduced directly into an Erlenmeyer flask and run in the same manner as the above.

AQUEOUS SODIUM PEROXIDE ABSORBENT.

Solutions of 1½% and 5% aqueous sodium peroxide were also used and run as stated above for the sulphite solution. Nos. 1 - 5 in each case were introduced through the L.P.G. Filler. The one marked "Blank" was measured out in a graduate cylinder and transferred directly to an Erlenmeyer flask.

ALCOHOLIC SODIUM SULPHITE ABSORBENT.

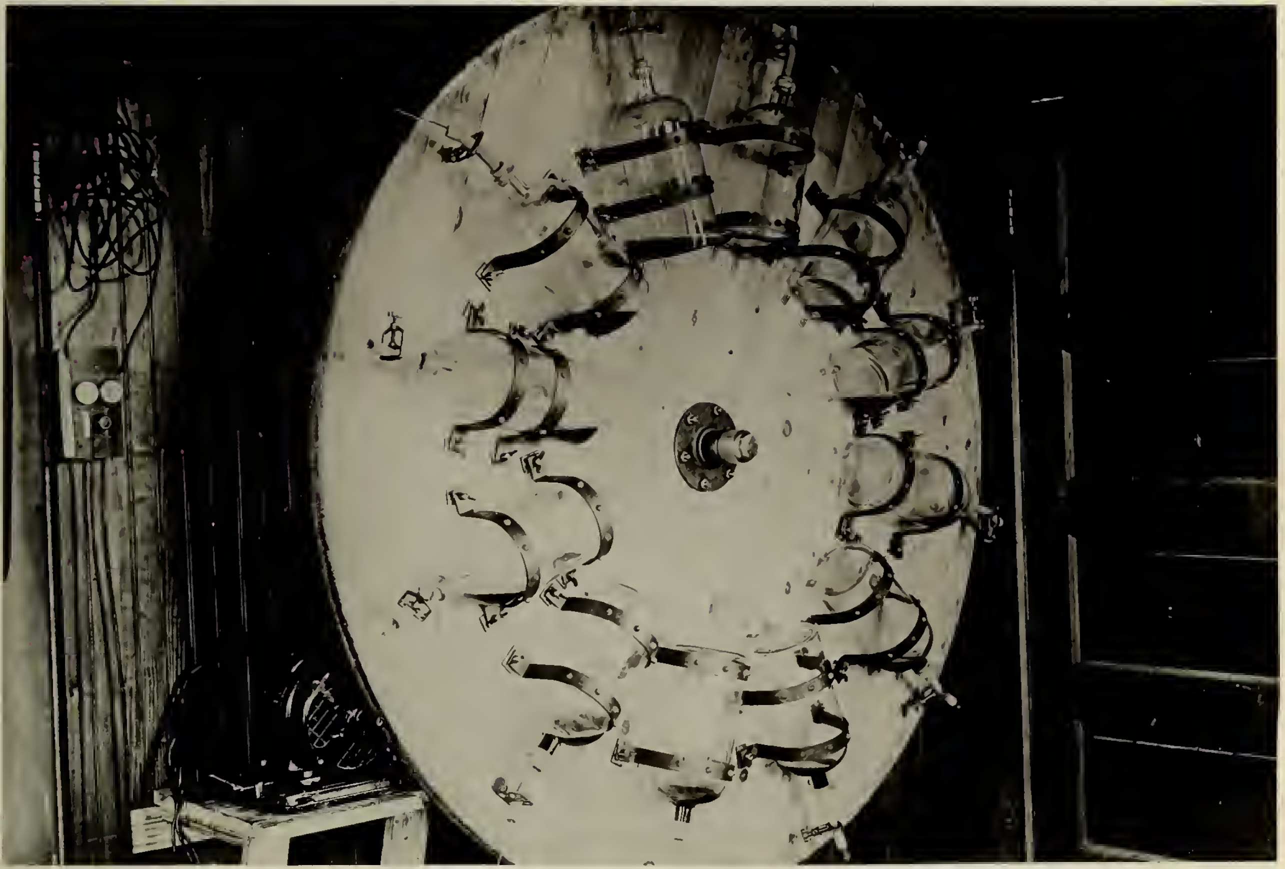
No.	CC.N/100 A_gNO_3 Added	CC.N/100 NaCNS Added	CC.N/100 A_gNO_3 Used	Difference in cc. between Blank & samples introduced thru L.P.G.Filler
Blank	9.35	9.09	0.26	None
1.	9.35	9.09	0.26	"
2	9.35	9.20	0.15	-.11
3	9.35	9.09	0.26	None
4	9.35	9.09	0.26	"
5	9.35	9.20	0.15	-.11

5% AQUEOUS SODIUM PEROXIDE ABSORBENT.

Blank	9.35	9.09	0.26	None
1	9.35	8.98	0.37	+.11
2	9.35	9.09	0.26	None
3	9.35	9.09	0.26	"
4	9.35	9.20	0.15	-.11
5	9.35	9.20	0.15	-.11

1½% AQUEOUS SODIUM PEROXIDE ABSORBENT.

Blank	9.35	9.20	0.15	None
1	9.35	9.20	0.15	"
2	9.35	9.09	0.26	+.11
3	9.35	9.20	0.15	None
4	9.35	9.20	0.15	"
5	9.35	9.20	0.15	"



PHOTOGRAPH NO. 9

Shaking Wheel.

For the analysis of a large number of gas samples collected in thefield or prepared in the laboratory, considerable time and energy is consumed in shaking the bottles. The shaking wheel (Photograph No. 9) eliminates the shaking of the bottles by hand and makes it possible to handle twelve samples at once. Each bottle receives identically the same amount of shaking that every other bottle does. In this way, it is possible to obtain strictly comparable results.

The shaking wheel consists of the wheel; brass binding straps and clamps; angle iron stops; the hub and wall support, and the electrical motor. The velocity of the wheel is regulated by means of friction drive. The speed of the wheel is so adjusted that the entire surface of the bottle is thoroughly washed by the absorbing solution.

2 Automatic Average Sampling Apparatus.

It is very desirable in many instances to obtain samples over a longer period of time which will give the average sample during a certain period. This is especially important where the concentration is very low. The Automatic Average Sampling Apparatus is designed to give samples over a longer period of time. Used in the open, during artillery fire, the apparatus must be protected by sand bags; in the trenches and dugouts no precautions are necessary.

The important points concerning the Average Sampling Apparatus are:

1. It is well suited for determining average

concentrations of gases.

2. By taking a larger sample a lower concentration of gas may be analyzed.

3. Each of the three tanks may be operated as a separate unit; or by using the gravity check valve, each tank may operate separately as part of one unit. Only one set of absorption bottles is then required.

4. The electromagnet tripping device automatically releases the plug and allows the water to run out.

5. The compact construction of the apparatus. The whole apparatus is fitted in an air tight wooden box to prevent corosive action of gases on the metal parts as much as possible.

The apparatus consists of three copper cylinders with a cone shaped top, terminating in a neck made to fit a No. 6 rubber stopper. Each cylinder has a capacity of twenty liters. The size of cylinder in use varied from 2 liters to 200 liters in capacity. Each stopper is fitted with a piece of glass tubing about 3 inches long, and by means of pressure rubber tubing is connected with its own valve on the gravity check valve. The gravity check valve is fastened in the corner of the box. From the check valve, another piece of rubber tubing connects with the absorption bottles. Leaving out the check valve each cylinder may be used as a separate unit, and having its own set of absorption bottles.

The whole apparatus is enclosed in a wooden box to prevent unnecessary exposure to corrosive gases. Photograph No. 10 A and B, shows the box and the copper cylinder

removed from the box. The magnet box (C) is made of sheet iron. It is fitted under the copper cylinders water tight.

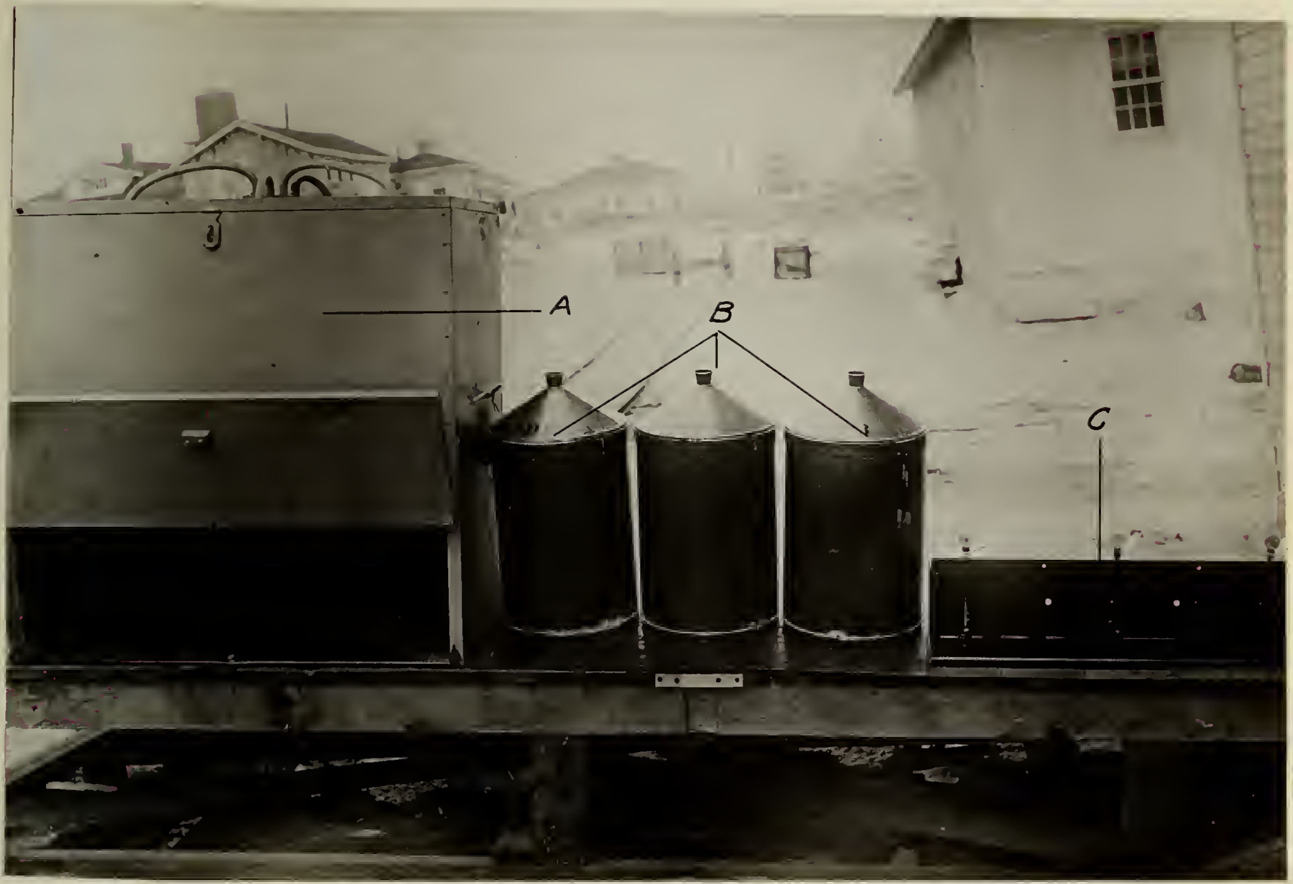
Plate No. 3 gives the details as to the construction and dimensions of the box and cans. In front near the bottom of the box is a hinged door. A sloping bottom beneath the copper cylinders serves to drain off the water as the cylinders are being emptied.

The bottom of each cylinder is fitted with a plug connected through a tripping device to an electromagnet. Photograph No. 11 is a near view of the magnet box, magnet and tripping device. Plate No. 4 gives the actual size of the magnet and the manner in which it is connected to the tank when the tripping device is in place. As stated above the magnet box is water tight and is not easily accessible. The magnet is adjusted by pulling the trip. (Plate 4). In doing this the plug at the bottom of the copper cylinder is placed in position. The cylinder is then ready to be filled with water, and connected to the absorption bottles. When the current passes through the magnet, the plug in the bottom of the cylinder is released and as the water runs out, an equal volume of air and gas is aspirated through the absorbing solution. The magnet is also provided with a circuit breaker which serves to test the current.

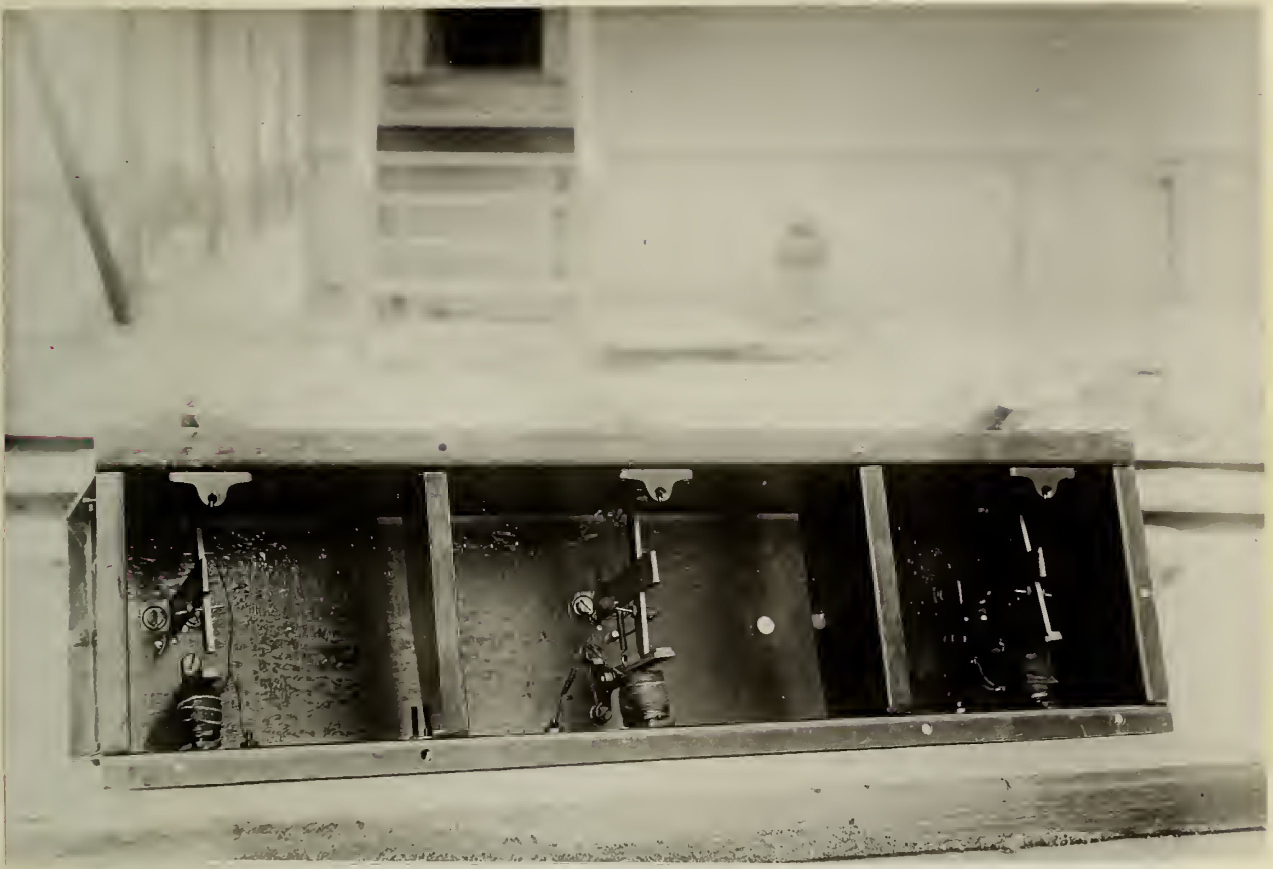
At first it was necessary to use one wash bottle for each cylinder, but the introduction of the gravity check valve made it possible to use only one set of absorption bottles for each apparatus. In low concentrations a sample three times as large is readily obtained.

The gravity check valve (Plate No. 5) consists of three superimposed brass plates, each four inches long and two inches wide by one quarter inch thick, andfour 1/4 inch copper tubes and valves numbered 0, 1, 2, 3, respectively. The check valves are in the copper tubes, and the latter also serve as the rubber tubing connections. The superimposed brass plates form an internal chamber through which the air passes when it is aspirated through the absorption bottle valve to the valve of the tank which is functioning. No. 0 is attached to the absorption bottles by means of tubing, and functions with either of the other three valves, each one of which is attached to the top of one of the copper cylinders by rubber tubing. When cylinder No. 1 is discharging water, air is drawn through the wash bottle, and valves No. 0 and No. 1, but valves Nos. 2 and 3 are closed. As soon as cylinder No. 1 has been emptied, valve No. 1 closes, and when cylinder No. 2 is opened, valve No. 2 is working while valves Nos. 1 and 3 remain closed. Each valve remains closed automatically and only when a current of air is drawn into the chamber formed by the brass plates, will air pass through any of the valves connected to the copper cylinders. Without the gravity check valve a separate set of absorption bottles must be used for each cylinder. If the copper cylinders were connected as a unit without the check valve, after cylinder No. 1 is empty, the air aspirated by cylinder No. 2 will not be drawn through the absorption bottle, but through cylinder No. 1. With the gravity valve this is impossible, as each valve closes as soon as the cylinder is empty. For

low concentrations this method of sampling is advantageous, because a sample three times as large is obtained. The sample will also represent the average concentration over a longer period of time.



PHOTOGRAPH NO. 10



PHOTOGRAPH NO. 11

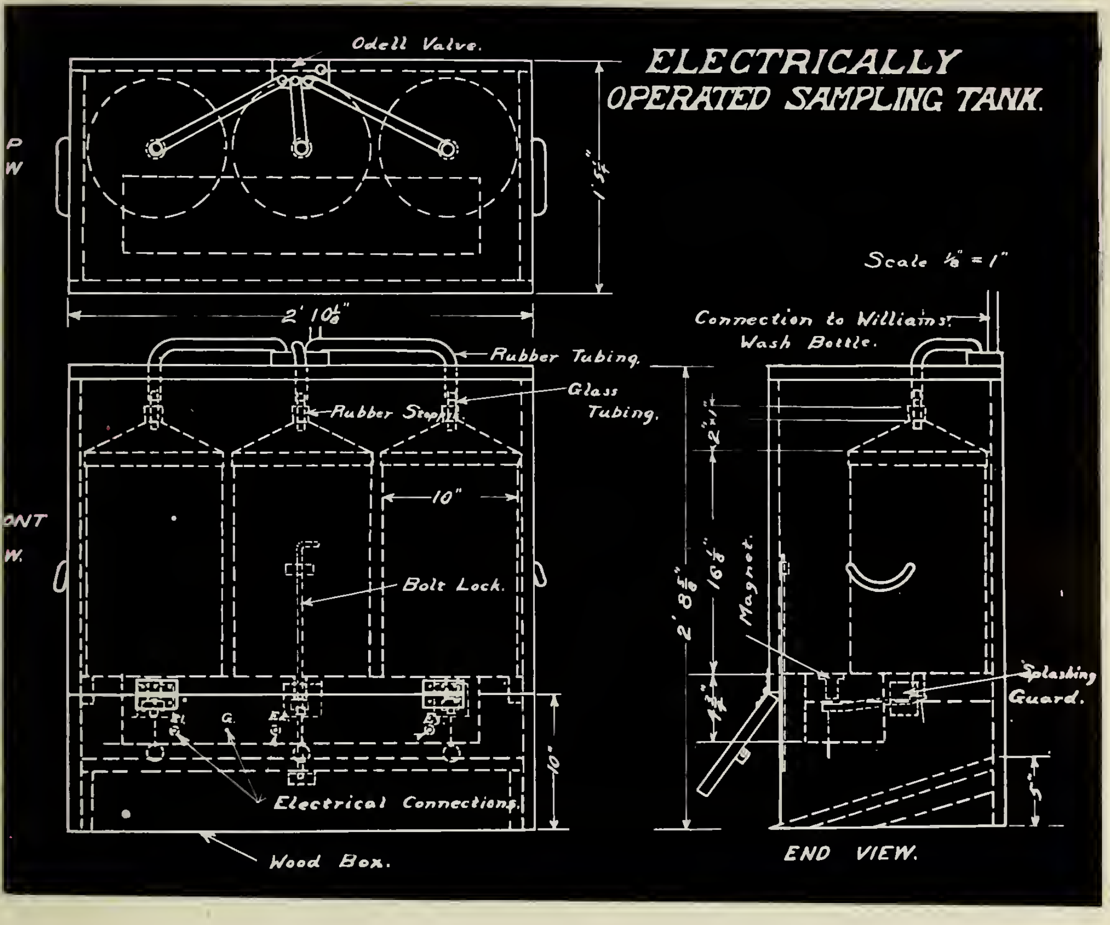
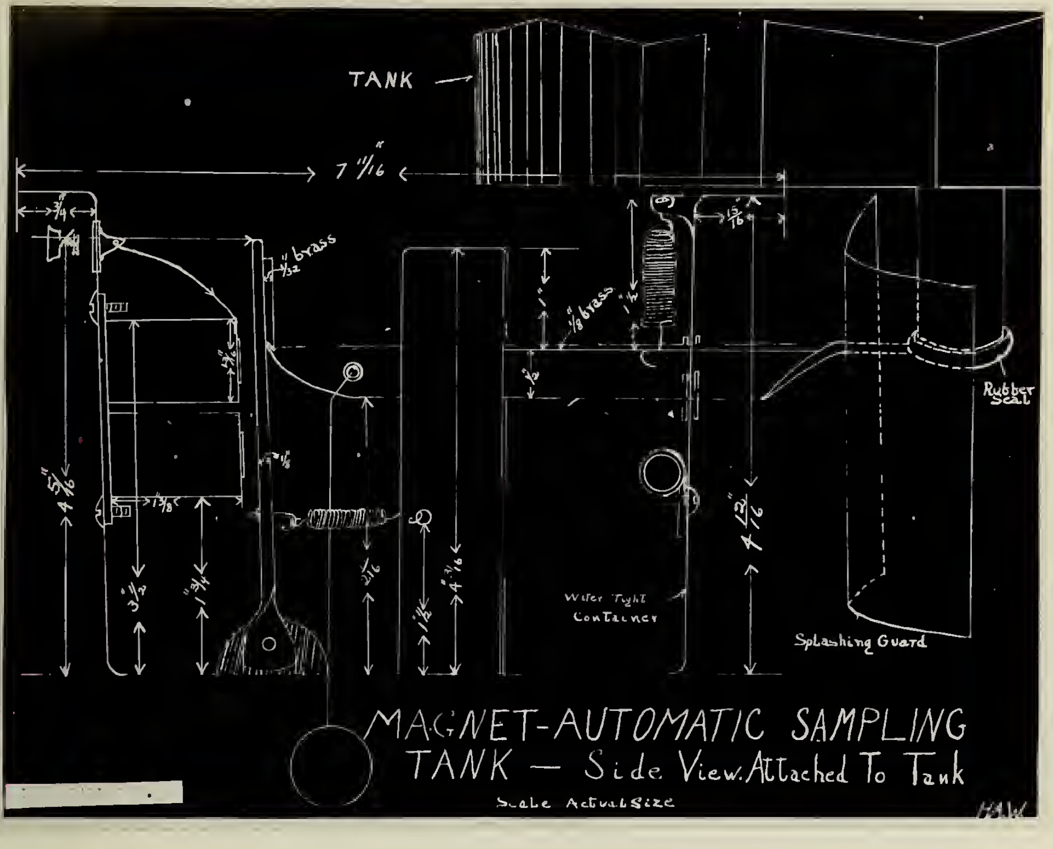

ELECTRICALLY OPERATED SAMPLING TANK.
Odell Valve.
P
W
1' 5¼"
Scale ⅛" = 1"
2' 10⅛"
Connection to Williams' Wash Bottle.
Rubber Tubing.
Glass Tubing.
Rubber Stopper.
10"
ONT
W.
Bolt Lock.
2' 8⅝"
16⅞"
2½"
1¾"
Magnet.
Splashing Guard.
10"
5"
G.
Electrical Connections.
Wood Box.
END VIEW.

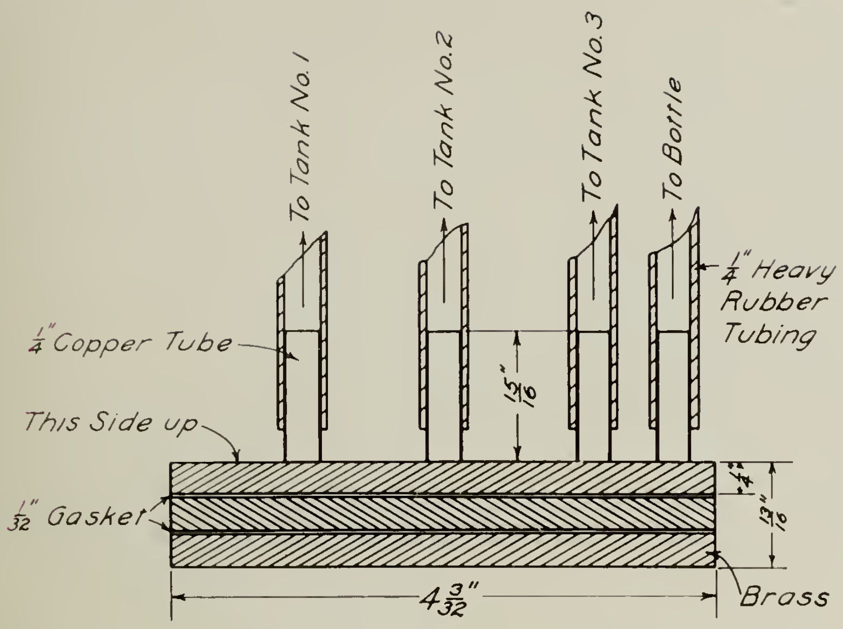
PLATE NO. 3



MAGNET-AUTOMATIC SAMPLING TANK — Side View. Attached To Tank

Scale Actual Size

PLATE NO. 4



The Gravity Check Valve

PLATE NO. 5

3. Hand Gas Sampling Pump.

The Pump is made of copper and is 15-¾" high and 10" in diameter. The essential parts of the pump are the tank, drum, and the two-way valve. The drum fits into the tank and an air tight connection is made with a water seal. By drawing the drum upward, air and gas is drawn into the drum through the valve and is confined under the drum. By connecting the two-way valve to an absorption bottle a measured volume of gas may be drawn through the absorbing solution as the drum is lifted.

The drum removed from the tank or pump is shown in Plate 6. The drum is fitted with a piston that fits into the cylinder of the pump. The outside of the piston at the bottom is very finely threaded. On this thread is fitted a diaphragm nut. By tightening or loosening this nut the capacity of the pump can be regulated from 5.7 liters to 6.7 liters per stroke.

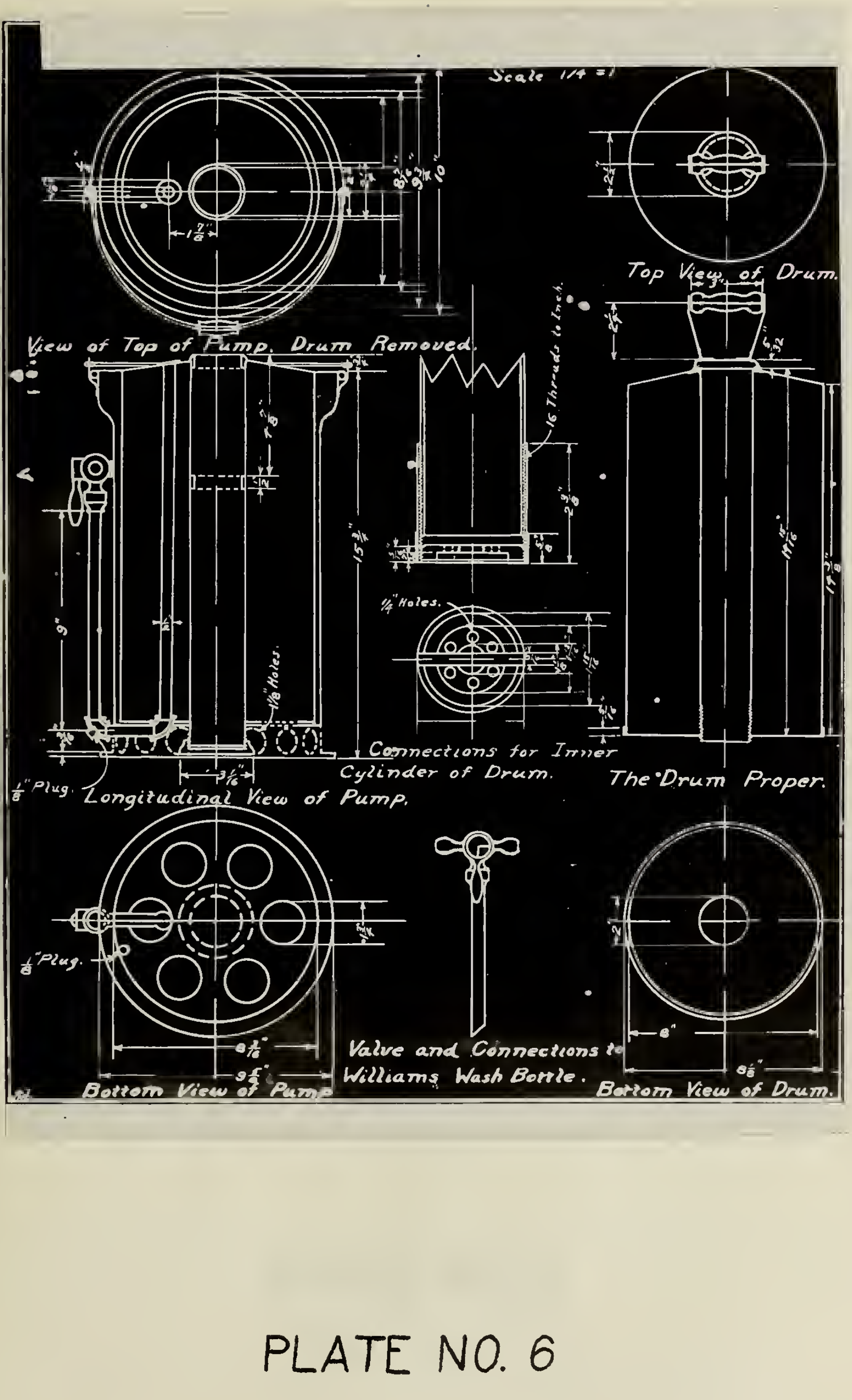
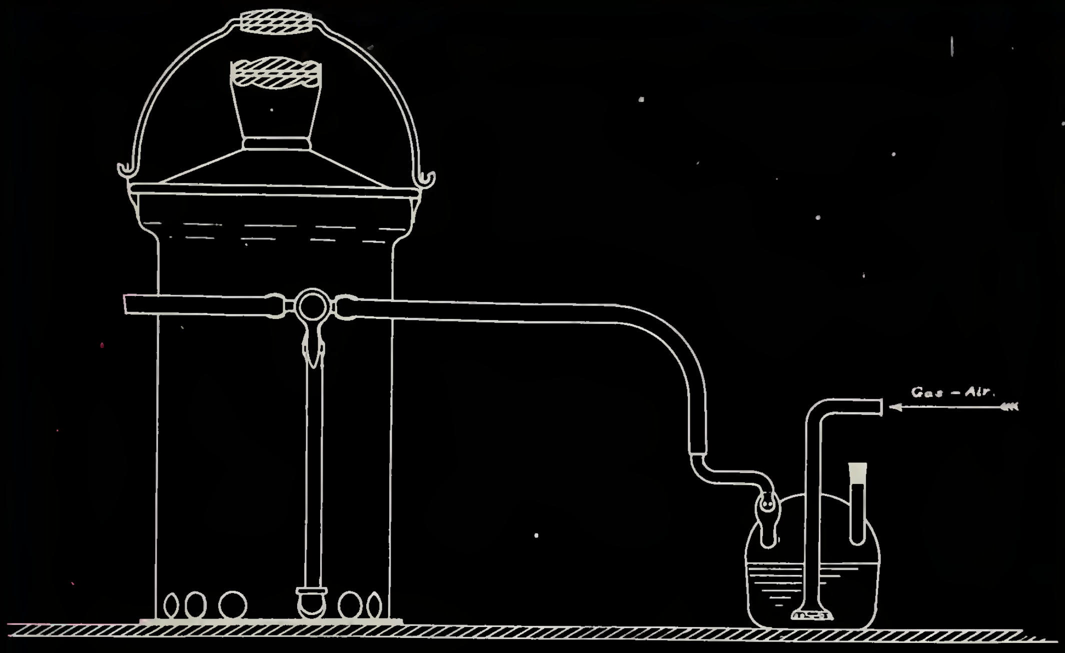

Scale 1/4 = 1
View of Top of Pump, Drum Removed.
1 7/8"
10"
Top View of Drum.
16 Threads to Inch.
1/4" Holes.
1/8" Holes.
15 3/4"
9"
Connections for Inner Cylinder of Drum.
The Drum Proper.
1/8" Plug.
Longitudinal View of Pump.
1/8" Plug.
Valve and Connections to Williams Wash Bottle.
Bottom View of Pump
Bottom View of Drum.
8"

PLATE NO. 6



GAS SAMPLING PUMP AND ABSORPTION BOTTLE.

PLATE NO. 7

The length of stroke can be increased 2-3/8" by loosening the nut. The drum cannot be removed from the pump unless the diaphragm nut on the piston is screwed off.

Water is used as the air seal between the tank and drum, the amount required is 1405 c.c. Any more water will cause trouble by some of it getting into the ½" intake pipe. From the top of the pump or tank (see Longitudinal View of Pump, Plate 6) to the bottom and making a bend is a ½" pipe, which comes up three-fourths of the way on the outside of the pump and ends in a two-way valve (See Valve Plate 7).

The pump must be carefully calibrated in the same manner in which it is to be used in taking samples. Varying the amount of absorbing solution, shape of absorption bottle, rate of drawing up the drum will seriously affect the results. The amount of absorbing solution is easily kept constant and so is the type of absorption bottle. The speed with which the air and gas are aspirated through the absorption bottles must not be so fast that some of the gas passes through unabsorbed. It should take 4 - 5 minutes to lift the drum with a slow steady pull so as to insure an even flow of gas through the absorbing solution. When the drum is lifted the full length of its stroke, the two-way valve is turned and the drum is slowly lowered, thus allowing the air to escape.

SUMMARY.

A systematic and efficient method of sampling and procedure for handling samples of gas concentrations in the field was developed and used with good results.

Concentrations of one gas or mixtures were automatically sampled by means of the electro magnet and evacuated bottle. A new vacuum bottle for field use was designed and used. A Filler for introducing absorbing solutions into a bottle containing a sample of gas without loss was perfected and used. For determing a very low gas concentration, the Automatic Average Gas Sampler was used. This apparatus was improved by using a gravity check valve, to give a sample over a longer period of time. The use of the Hand Sampling Pump also gave the average concentration for a certain position. The Pump could be operated continuously as long as the gas cloud was present.

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